PB-215 887

Validation of Improved Chemical Methods for Sulfur Oxides Measurements from Stationary Sources

Walden Research Corp.

prepared for

Environmental Protection Agency

NOVEMBER 1972

Distributed By:

NTIS

National Technical Information Service
U. S. DEPARTMENT OF COMMERCE

EPA-R2-72-105
November 1972

PB 215 887

Environmental Protection Technology

Validation of Improved Chemical Methods for Sulfur Oxides Measurements from Stationary Sources

NATIONAL TECHNICAL
INFORMATION SERVICE

Office of Research and Monitoring
U.S. Environmental Protection Agency
Washington, D.C. 20460

258

EPA-R2-72-105

Validation of Improved Chemical Methods for Sulfur Oxides Measurements from Stationary Sources

By

J. Driscoll, J. Becker,
R. Hebert, K. Horbal and M. Young
Walden Research Corporation
359 Allston Street
Cambridge, Massachusetts

Contract No. 68-02-0009
Program Element No. A11010

Project Officer: Fredric C. Jaye

Division of Chemistry and Physics
National Environmental Research Center
Research Triangle Park, North Carolina 27711

Prepared for

OFFICE OF RESEARCH AND MONITORING
U.S. ENVIRONMENTAL PROTECTION AGENCY
WASHINGTON, D.C. 20460

November 1972

This report has been reviewed by the Environmental Protection Agency and approved for publication. Approval does not signify that the contents necessarily reflect the views and policies of the Agency, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

BIBLIOGRAPHIC DATA SHEET

1. Report No.
EPA-R2-72-105

2.

3. Recipient's Accession No.
PB-215 887

4. Title and Subtitle
Validation of Improved Chemical Methods for Sulfur Oxides Measurements from Stationary Sources

5. Report Date
November 1972

6.

7. Author(s)
J. Driscoll, J. Becker, R. Hebert, et al

8. Performing Organization Rept. No.

9. Performing Organization Name and Address
Walden Research Corporation
359 Allston Street
Cambridge, Massachusetts

10. Project/Task/Work Unit No.

11. Contract/Grant No.
68-02-0009

12. Sponsoring Organization Name and Address
U.S. ENVIRONMENTAL PROTECTION AGENCY
Office of Research and Monitoring
Washington, D. C.   20460

13. Type of Report & Period Covered

14.

15. Supplementary Notes

16. Abstracts
The principal objective of this program was to validate the following wet chemical methods for sulfur oxides: the barium chloranilate procedure, the barium ion-thorin procedure, and lastly, a simplified method, which is not specific for sulfate, which was also used to analyze aliquots of the SO_2 samples. The first phase of the program was planned to evaluate the collection and analysis methods. During second phase, the revised chemical methods were tested at uncontrolled coal, uncontrolled oil, and controlled coal-fired power plants. A modification to the program enabled the data collected in the field to be utilized in preparing the national emission standards for sulfur oxides. The results obtained in fossil fuel-fired power plants and in the Walden pilot plant are given in Section 1. Section 2 discusses the results for the other (non-combustion) stationary sources. For each source tested, a brief description of the process is provided. The appendix contains a detailed write-up of the analytical methods used, the Pb titration method developed under this contract and data obtained on solid sorbents for collection of SO_x.

17. Key Words and Document Analysis. 17a. Descriptors

Air pollution
Sulfur oxides
Combustion
Sources
Fossil fuels
Electric power plants
Pilot plants
Sampling
Chemical analysis
Barium

17b. Identifiers/Open-Ended Terms

Air pollution measurement
Stationary sources
Wet chemical methods
Barium chloranilate
Barium ion-thorin

17c. COSATI Field/Group   13B

18. Availability Statement
Unlimited

19. Security Class (This Report)
UNCLASSIFIED

20. Security Class (This Page
UNCLASSIFIED

21. No. of Pages
258

22. Price
$6.[illegible]5

ii-b

ACKNOWLEDGMENTS

We are pleased to acknowledge the assistance of F. Jaye, R. Larkin, and R. Statnick of EPA for their help in the planning phase of this program. We are indebted to Drs. Miller, Scott and Thompson also of EPA for performing X-ray fluorescence and emission spectrographic analyses of selected field samples. We thank the many organizations which provided the test sites for the SO_x validation program.

PROJECT STAFF

Major technical contributions to this report have been made by the following:

J. Driscoll - Program Manager
J. Becker
J. Ehrenfeld
P. Giever
P. Gravalese
R. Hebert
K. Horbal
R. Maddock
L. Paley
M. Young

SECTION 1

FOSSIL FUEL COMBUSTION SOURCES

TABLE OF CONTENTS

Section | Title | Page

1.1 INTRODUCTION 1-1

1.2 BRIEF DESCRIPTION OF SO_x EMISSIONS FROM FOSSIL FUEL COMBUSTION 1-4

1.3 SAMPLING SYSTEMS AND ANALYTICAL METHODS 1-10

- 1.3.1 Probe 1-10
- 1.3.2 Sampling Trains 1-14
- 1.3.3 Calibration of Metering Devices and Variation with Time 1-18
- 1.3.4 Analytical Methods 1-18

1.4 SO_2 TEST RESULTS FOR A CONTROLLED COAL-FIRED POWER PLANT 1-25

1.5 SO_2 RESULTS FOR AN OIL-FIRED POWER PLANT 1-34

1.6 SO_2 RESULTS FOR AN UNCONTROLLED COAL-FIRED POWER PLANT .. 1-41

1.7 SO_3 RESULTS FROM FOSSIL FUEL COMBUSTION SOURCES 1-58

1.8 SO_2 RESULTS OBTAINED IN THE WALDEN PILOT PLANT AND LABORATORY 1-61

- 1.8.1 Description of Pilot Plant 1-61
- 1.8.2 Supplementary Laboratory and Pilot Plant Studies . 1-61
- 1.8.3 Effect of NO_x on SO_2 Methods and Accuracy Studies 1-71
- 1.8.4 Effect of HCl on the Accuracy of SO_2 Methods 1-82
- 1.8.5 Effect of Organic Acids on SO_2 Methods 1-93

1.9 SUMMARY AND CONCLUSIONS 1-99

LIST OF ILLUSTRATIONS

Figure | Caption | Page

1-1 Actual Test Schedule 1-3

1-2 Schematic of Stationary Combustion Systems 1-7

1-3 Probe Module 1-12

1-4 SO_x-NO_x Sampling Probe and Condenser 1-13

Preceding page blank

LIST OF ILLUSTRATIONS (continued)

Figure	Caption	Page
1-5	Sampling Trains	1-15
1-6	Controlled Condensation Collector for SO_3	1-16
1-7	Walden Prototype Sampling System	1-17
1-8	Flow Chart of Analytical Procedures	1-21
1-9	Effect of Cation Exchange Resin on the Removal of Sulfate	1-24
1-10	Sampling Port Locations for Controlled Coal-Fired Power Plant	1-26
1-11	Schematic of the Oil-Fired Power Plant	1-35
1-12	Detail of Test Ports in an Oil-Fired Power Plant	1-36
1-13	Uncontrolled Coal-Fired Power Plant	1-47
1-14	Sampling Port Locations for the Uncontrolled Coal-Fired Power Plant	1-48
1-15	Walden Pilot Plant	1-62
1-16	Pilot Plant Test Section Assembly	1-63
1-17	Pilot Plant Schematic	1-64
1-18	Linearity of the Calibration Curve for the Barium Chloranilate Method	1-68
1-19	Effect of Flushing Time on the SO_2 in 80% IPA	1-70
1-20	Equilibrium Distribution of Chlorine Compounds in the Combustion Gas of a Sewall Coal at 20 Percent Excess Air	1-88
1-21	Doping System for Organic Acids	1-95

LIST OF TABLES

Table	Title	Page
1-1	Nationwide Emissions of SO_x, 1966	1-5
1-2	Nationwide Emissions of SO_2 from Fossil Fuel Combustion Sources (1967)	1-6
1-3	Size Categories for Stationary Combustion Sources	1-8
1-4	Emission Parameters for Fossil Fuel Combustion	1-9
1-5	SO_x Control Systems	1-11

LIST OF TABLES (continued)

Table	Title	Page
1-6	Comparison of Rated and Measured Flow Rates for Some Millipore Critical Orifices	1-19
1-7	Variation of Orifice Calibration with Sampling Time in the Field	1-20
1-8	Effect of Ion Exchange Step on the Analytical Methods	1-23
1-9	SO_2 Test Results from a Controlled Coal-Fired Power Plant at the Inlet of a Wet Scrubber	1-27
1-10	Fuel Analysis for Controlled Coal-Fired Power Plant	1-28
1-11	SO_2 Test Results from a Controlled Coal-Fired Power Plant at the Outlet of a Wet Scrubber	1-30
1-12	Precision of Duplicate Analysis of SO_2 for a Controlled Coal-Fired Power Plant	1-32
1-13	Regression Analyses and Correlation Coefficients for a Controlled Coal-Fired Power Plant	1-33
1-14	SO_2 Test Results from an Oil-Fired Power Plant	1-37
1-15	Precision of Duplicate SO_2 Analysis for an Oil-Fired Power Plant	1-39
1-16	Regression Analyses and Correlation Coefficients for an Oil-Fired Power Plant	1-40
1-17	Fuel Analysis for an Oil-Fired Power Plant	1-42
1-18	Supplementary Field Test Data for an Oil-Fired Power Plant	1-43
1-19	Comparison of Measured and Calculated SO_2 Values for an Oil-Fired Power Plant, Barium Chloranilate Method	1-44
1-20	Comparison of Measured and Calculated SO_2 Values for an Oil-Fired Power Plant, Ba^{++} Titration Method	1-45
1-21	Comparison of Measured and Calculated SO_2 Values for an Oil-Fired Power Plant, NaOH Titration Method	1-46
1-22	SO_2 Test Results from an Uncontrolled Coal-Fired Power Plant	1-50
1-23	Precision of Duplicate SO_2 Analysis for an Uncontrolled Coal-Fired Power Plant	1-51
1-24	Regression Analyses and Correlation Coefficients for an Uncontrolled Coal-Fired Power Plant	1-52
1-25	Supplementary Field Test Data for an Uncontrolled Coal-Fired Power Plant	1-53

LIST OF TABLES (continued)

Table	Title	Page
1-26	Fuel Analyses for an Uncontrolled Coal-Fired Power Plant	1-54
1-27	Comparison of Measured and Calculated SO_2 Values from an Uncontrolled Coal-Fired Power Plant, Barium Chloranilate Method	1-55
1-28	Comparison of Measured and Calculated SO_2 Values from an Uncontrolled Coal-Fired Power Plant, Ba^{++} Titration Method	1-56
1-29	Comparison of Measured and Calculated SO_2 Values from an Uncontrolled Coal-Fired Power Plant, NaOH Titration Method	1-57
1-30	SO_3 Test Results for Fossil Fuel Combustion	1-60
1-31	Pilot Plant Specifications	1-65
1-32	Characteristics of the Pilot Plant on #2 Oil and Gas	1-66
1-33	Effect of Flushing Time on the SO_2 Concentration in the 80% Isopropanol-20% Water Absorber	1-69
1-34	Effect of NO_x on Wet Chemical Methods for SO_2	1-72
1-35	Determination of Collection Efficiency of SO_2 in Aqueous Hydrogen Peroxide Solution	1-75
1-36	Pilot Plant Comparison of Theoretical SO_2 versus ppm SO_2 Measured by Wet Chemistry	1-77
1-37	Pilot Plant Results - Precision with NO_x Doping	1-83
1-38	Regression Equations and Correlation Coefficients for a Gas-Fired Pilot Plant	1-84
1-39	Chlorine Content of Various Coals	1-86
1-40	Combustion of Pulverized Coals	1-87
1-41	Comparison of Measured and Calculated HCl Concentrations in the Pilot Plant	1-90
1-42	Effect of HCl on Wet Chemical Methods for SO_2	1-91
1-43	Pilot Plant Doping - Precision of HCl and HOAc Doping	1-94
1-44	Effect of Organic Acids on Wet Chemical Methods for SO_2	1-96

1.1 INTRODUCTION

This program was initiated in January 1971. The principal objective was to validate the wet chemical methods for sulfur oxides which were developed under EPA Contract No. CPA 22-69-95. A brief description of the methods is given below:

The barium chloranilate procedure contain the following major recommendations:

(a) SO_3 is separated from SO_2, water, and other interferences by controlled condensation of the flue gas.

(b) SO_3 and SO_2 analyses are performed colorimetrically.

(c) Sampling rates are controlled by critical orifice.

The barium ion-thorin procedure has been used as a standard for comparison. This has been described in detail by EPA (1971) and is summarized in Appendix I. The principal differences in this procedure are that SO_3 is collected by absorption in 80% isopropanol-20% water and analysis is, of course, conducted by titration.

A simplified method, which was not specific for sulfate, was also used to analyze aliquots of the SO_2 samples. This method involves titration of the sulfuric acid with standard sodium hydroxide solution using bromphenol blue indicator. This procedure is also described in Appendix I.

The reader is referred to the Final Report under EPA Contract No. CPA 22-69-95, "Improved Chemical Methods for Sampling and Analysis .....," Volume I - Sulfur Oxides, APTD #1106, PB 209-268, for background material on the chemistry as well as the collection and analysis methods for sulfur oxides.

The first six months of the program were initially planned to evaluate (determine accuracy, interferences, etc.) the collection and analysis methods in the pilot plant and define an experimental plan for the field testing program. During the last six months of the program, the revised methods would then be tested at uncontrolled coal, uncontrolled oil, and controlled coal-fired power plants.

At the end of February 1972, a meeting was held at EPA in Durham, North Carolina. Representatives of Walden Research Corp., the EPA Project Officer, and the EPA source testing group were present. It was decided that the program should be modified to enable the data collected in the field to be utilized in preparing the national emission standards for sulfur oxides.

As a result of the new schedule, major modifications to the program involved:

(a) Interchanging the position of the pilot plant and field programs - *the field program would now be completed before the pilot plant studies.*

(b) Reducing the elapsed time in the field from six months to less than two. This would be done by overlapping test programs at the various sites.

(c) Presentation of the test data including statistical analysis by the last week in April 1971.

The field testing was completed and the report was presented by the prescribed time. Some difficulties were encountered as a result of the speeded-up program. These will be discussed in the text.

Following the field program, the pilot plant studies were initiated. Before these were completed, a request was made by EPA to extend the scope of the SO_x validation program to include several Category II and other stationary sources. These were:

(a) gray iron foundries
(b) kraft pulping
(c) iron and steel
(d) smelting
(e) sulfuric acid

A detailed schedule of the actual resulting expanded test program is given in Figure 1-1.

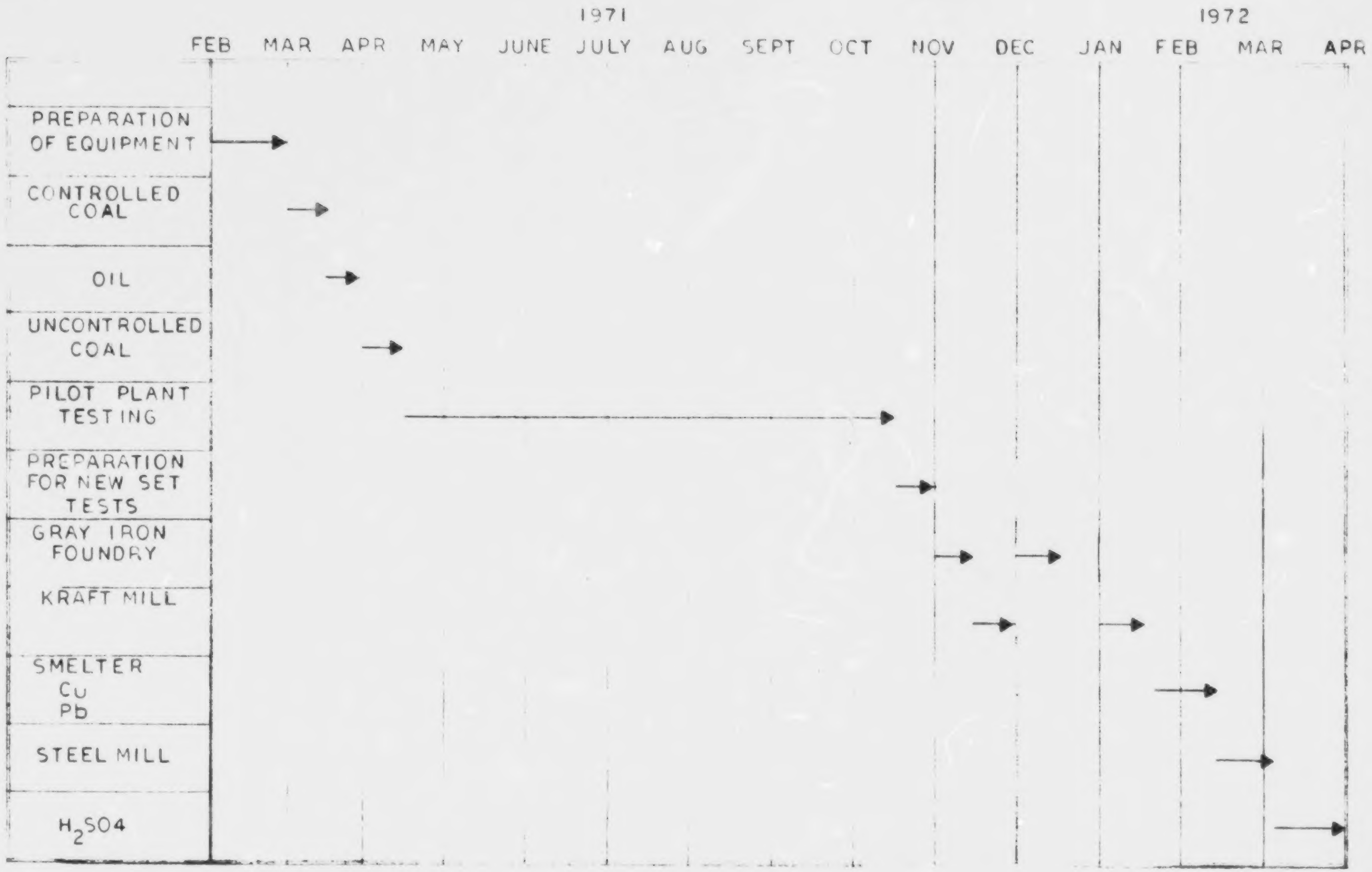


Figure 1-1. Actual Test Schedule.

The results obtained in fossil fuel-fired power plants and in the Walden pilot plant are given in Section 1. The results for the other (non-combustion) stationary sources are discussed in Section 2. The appendix contains a detailed write-up of the analytical methods used, the Pb titration method developed under this contract, and data obtained on solid sorbents for collection of SO_x.

For each source which was tested, a brief description of the process is given to enable the reader to understand the sampling and/or analytical configurations used. This section is followed by a description of the sampling and analytical procedures, the test data including statistical analysis, and conclusions and recommendations for each source.

1.2 BRIEF DESCRIPTION OF SO_x EMISSIONS FROM FOSSIL FUEL COMBUSTION*

A rough guide to method development priorities may be obtained from the relative contributions of various sources to national SO_x emissions (Table 1-1).

Since SO_x emissions are primarily fuel dependent rather than equipment dependent, the data of Table 1-1 essentially integrate the product of fuel use and do not distinguish fossil fuel effluents from process emissions.

A somewhat more detailed breakdown, which excludes (direct-fired) process emissions, is available from work conducted at Walden under EPA contract (Ehrenfeld, et al., 1971) and is given in Table 1-2.

As may be seen from the Boiler Category of Table 1-2, 90% of total (non-process) emissions are attributable to watertube boilers, for which the smallest size range is about 25,000 pounds of steam per hour (or ca. 3×10^7 Btu/hr). The SO_2 emissions determination problem is centered in these relatively large sources. Further examination of the categories of Tables 1-1 and 1-2 reveals that the highest priority is clearly to be placed upon

---

*This section was taken from Driscoll and Berger (1971).

TABLE 1-1

NATIONWIDE EMISSIONS OF SO_x, 1966

		10^6 tons/year
Total from Fossil Fuel Combustion in Stationary Sources		22.1
By Fuel	Coal	18.3
	Residual Fuel Oil	3.3
	Distillate Fuel Oil	0.5
By Sector	Power Generation[a]	14.0
	Industrial	5.6
	Residential and Commercial Heating	2.5

---

[a] About 90% of the power generation contribution to SO_x emission is derived from coal-fired units and about 10% from oil.

TABLE 1-2

NATIONWIDE EMISSIONS OF SO_2 FROM FOSSIL FUEL COMBUSTION SOURCES (1967)

		10^6 tons/year
Total from Fossil Fuel Combustion in Stationary Sources		18.63
By Fuel	Coal	15.60
	Residual Fuel Oil	2.76
	Distillate Fuel Oil	0.27
By Sector	Utilities	12.58
	Industrial	4.28
	Commercial	1.53
	Residential	0.24
By Boiler Category (excluding residential)		
	Watertube ≥ 500,000 pph	9.29
	Watertube ≤ 500,000 pph	6.50
	Firetube	0.88
	Cast Iron	0.72

analytical methods and equipment applicable to large boilers since they represent the largest sources and will involve the first application of control techniques.

It does not appear desirable to develop specially adapted high precision methods applicable to the myriad and relatively unimportant small sources at this time.

A prerequisite for the selection of manual chemical methods for sampling and analysis of gaseous pollutants from the combustion of fossil fuels is the description of the environments to be sampled. These will be discussed in the following paragraphs.

All combustion equipment can be generalized in terms of the schematic shown in Figure 1-2. Fuel is burned in a furnace to release heat. Combustion products and ash are generated as undesirable by-products. The combustion heat is transferred in a heat exchanger to some convenient thermal fluid, usually water, steam or air. Domestic heaters are familiar, simple examples of this generalized system. They are designed to provide unattended service over long periods of time to untrained users. Consequently, they are characterized by a low level of sophistication in combustion control, heat transfer (thermal efficiency) or air pollution control. On the

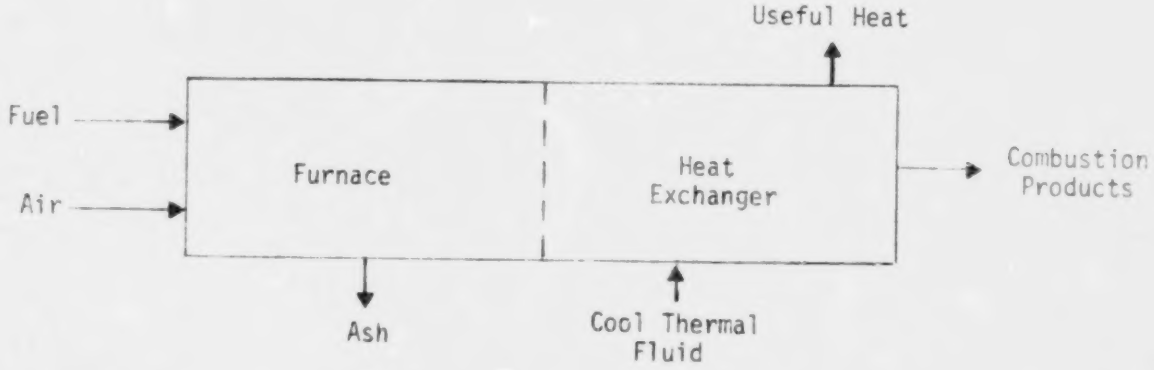


Figure 1-2. Schematic of Stationary Combustion Systems.

other end of the sophistication spectrum are new steam generating units at large power plants. While the generalized combustion system shown in Figure 1-2 is still applicable, it is embellished considerably by combustion air preheaters, economizers, high pressure heat exchangers and pollution control equipment. In addition, computerized systems are utilized to monitor and control furnace and heat exchanger operation. The combustion products may be modified by the use of additives, either in the fuel, or added in the furnace or heat exchangers.

For this evaluation, we have divided combustion equipment into three arbitrary size groups, as shown in Table 1-3, according to several approximately equivalent criteria. There are relatively few suppliers of equipment in the large size range (four major sources) with 1968 annual sales of the order of 75 units. On the other hand, there are several hundred suppliers of small units with 1967 annual shipments of approximately 1,500,000 units. Useful life is perhaps 15 and 30 years, respectively, for the small and large units. Combining the large number of installed units with the disparate designs, range of fuels used, load factors, varying operating practices, etc., it is clear that it is totally impractical to attempt to specify the environment for individual cases. Rather, we have reviewed the range of environments reported in the literature for each of the three size categories shown in Table 1-3 for oil, coal and gas. A summary of emission parameters is given in Table 1-4 in consistent units ($\#/10^6$ Btu).

TABLE 1-3

SIZE CATEGORIES FOR STATIONARY COMBUSTION SOURCES

	Large	Intermediate	Small
Btu per hour	$\geq 5 \times 10^8$	$3\times10^5-5\times10^8$	3×10^5
Boiler horsepower	$\geq$ 15,000	10-15,000	< 10
Pounds of steam per hour	$\geq$ 500,000	350-500,000	< 330
Megawatts	$\geq$ 50	< 50 MW	Not Applicable

TABLE 1-4

EMISSION PARAMETERS* FOR FOSSIL FUEL COMBUSTION[a] (pounds/10^6 Btu)

	GAS[b]			OIL[c]			COAL[d]		
	Large	Intermed.	Small	Large (Resid.)	Intermed. (Resid./Dist.)	Small (Dist.)	Large	Intermed.	Small
Velocity ft/min	2000-3000			2000-3000			2000-3000		
Moisture	18% @ 0% XS Air ----- 15% @ 20% XS Air ------			10% @ 0% XS Air ----- 9% @ 20% XS Air ------			----- 6% (Nominal) ------		
Excess Air %	15	15-75	75	20	20-75	75	25	25-75	75-100
Stack Temp. °F (of Breeching)	275-400	400-750	750-900	300-400	400-750	750-900	300-400	400-750	750-900
CO	Neg.	4×10^{-4}	4×10^{-4}	3×10^{-4}	0.01/0.01	.01	0.02	0.1-2	2
SO_2	4×10^{-4}	4×10^{-4}	4×10^{-4}	1.65	1.65/0.31	0.31	3.5	3.5	3.5
SO_3				0.03	$0.016/3 \times 10^{-3}$	3×10^{-3}			
NO	0.35	0.2	0.1	0.68	0.47/0.51	.08	0.8	0.8-0.3	0.3
NO_2									
Particulate	0.014	0.016	0.017	0.07	0.15/0.10	0.06	0.46 (90% cont.)	0.53 (65% cont.)	0.8 (uncont.)
Hydrocarbons	Neg.	Neg.	Neg.	0.022	0.01/0.01	.02	8×10^{-3}	0.04-0.4	0.4
Transients	10% of Capacity Per Min.			10% of Capacity Per Min.			5% Capacity Per Min.		

a. Details in Appendix 1, Final Report, Vol. I

b. 1100 Btu/SCF

c. $S_{dist.}$ 0.39%, 142,000 Btu/gal
$S_{resid.}$ 1.6%, 152,000 Btu/gal

d. S = 2.5%, 8% ash, 13,000 Btu/#

*From Driscoll and Berger (June 1971).

Details are given in Appendix I from Driscoll and Berger (1971). A summary of conditions before and after control equipment for the most prominent SO_x control systems is given in Table 1-5. From these data, the various requirements for principal factors such as required sensitivity, possible interferences, transients and temperature regimes may be determined. The major factors are briefly described below.

Sampling equipment must be designed to tolerate "normal" operation as well as unusual temperature excursions. In general, large units are designed for stack temperatures of 300-400°F. Gas-fired unit emissions, as a result of their freedom from the effects of corrosive sulfuric acid mist, run cooler, about 275°F. In domestic units, stack temperatures are much higher, ca. 700-800°F. Inlet temperatures of the Monsanto SO_x control process also run at this level. Intermediate combustion units cover the range of temperatures between these extremes (400-700°F).

The implications of this temperature variation for sampling are threefold:

(1) Materials of construction must be adequate to tolerate the highest temperature.

(2) Materials must be chosen to eliminate high temperature catalytic oxidation of SO_2 to SO_3 in the sample probe and lines.

(3) Water and acid condensation must be taken into consideration in design of the sampling train. The sample stream should be kept hot insofar as possible, up to the collection equipment.

1.3 SAMPLING SYSTEMS AND ANALYTICAL METHODS

1.3.1 Probe

The probe, Figure 1-3, consists of an electrically heated pyrex insert with a stainless steel jacket. A detailed drawing of the probe and sampling system is shown in Figure 1-4. The probe could be heated to a temperature of about 330°F with 120 VAC. A loosely-packed glass-wool plug

TABLE 1-5

SO_x CONTROL SYSTEMS

Developer	Process	BEFORE			AFTER	
		Temp. ^{o}F	Input	Temp. ^{o}F	Output	SO_x*
CE	Wet Scrubbing (Dolomite)	250-300	Normal Double Load Particulates	250-300	99% Particulate Removal	SO_3-99% Removed SO_2-90% Removed
Monsanto	CAT-OX	850	Follows 99% + Elect. Precip.	250	--	(Same)
Bumines	Alkalized Alumina	625	Recommend 0.9 gr/ft^3	250	Follows Cyclone Separator	(Same)
Reinluft	Char. Absorption	250-300	Recommend 0.9 gr/ft^3	250	--	(Same)
Wellman-Lord	Alkali-Sulfite Absorption	300	Only as Req'd by Power Plant Equipment	250	+95% Particulate Removal by Special Scrubber	(Same)
TVA	Dry Dolomite Absorption (Intermittent)	Additive Rate of 2 Times Stoichiometric Requirement	2-3 times Particulate Load in Flue Gas Stream and Bottom Ash			25-50% SO_2 99% SO_3

---

*Design efficiencies assumed

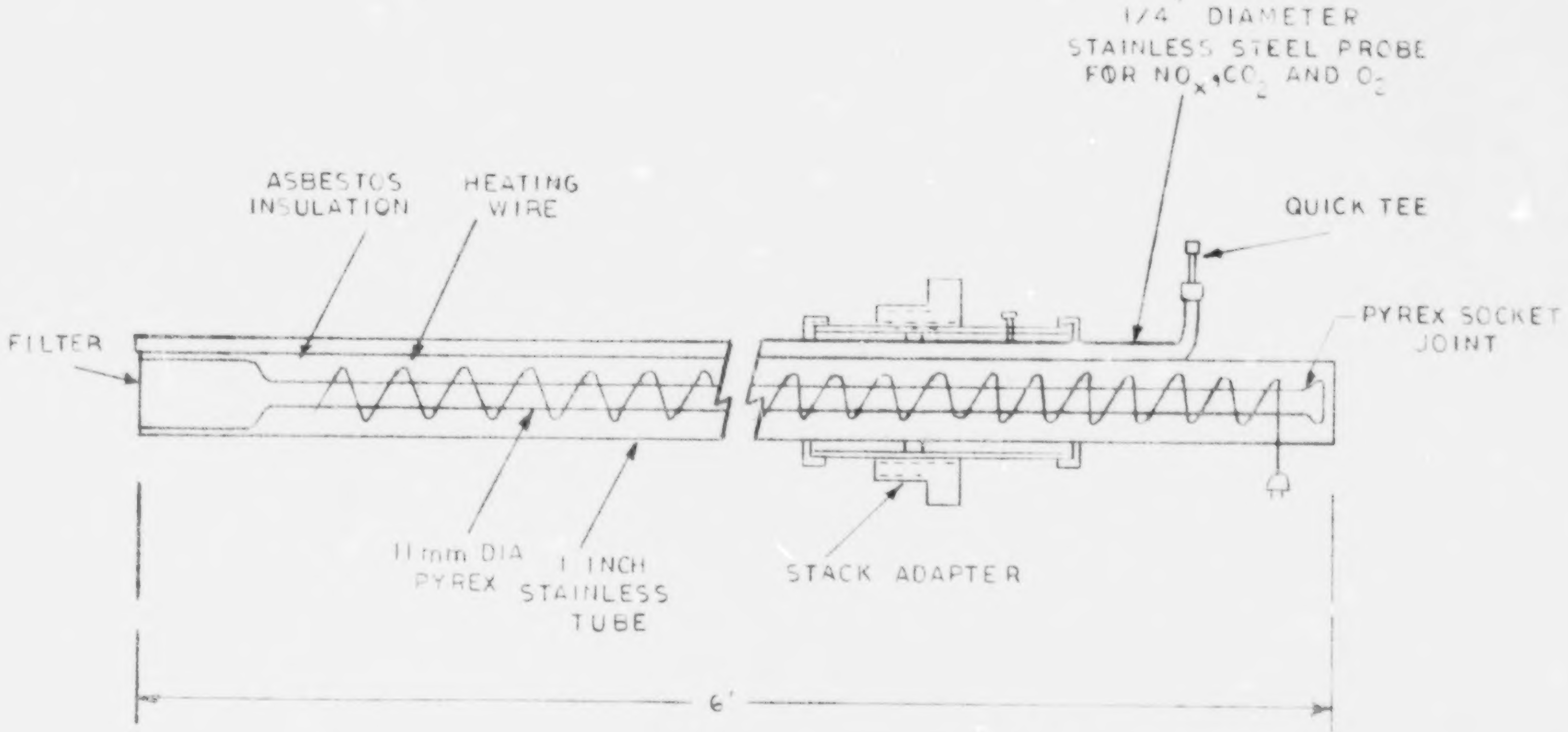

1/4" DIAMETER
STAINLESS STEEL PROBE
FOR NO_x, CO_2 AND O_2
ASBESTOS INSULATION
HEATING WIRE
QUICK TEE
FILTER
PYREX SOCKET JOINT
11mm DIA PYREX
1 INCH STAINLESS TUBE
STACK ADAPTER
6'

Figure 1-3. Probe Module.

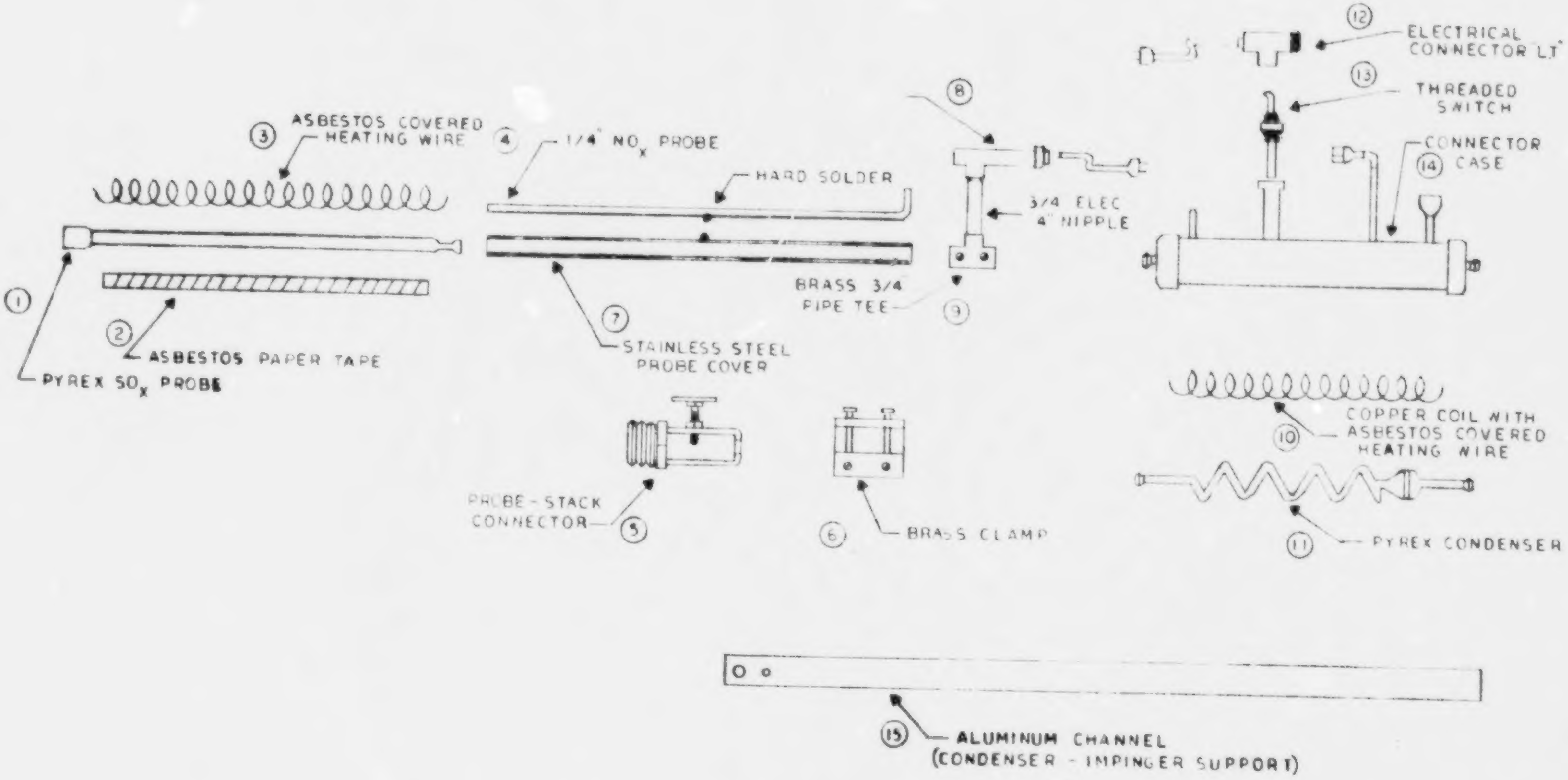

① PYREX SO_x PROBE
② ASBESTOS PAPER TAPE
③ ASBESTOS COVERED HEATING WIRE
④ 1/4" NO_x PROBE
HARD SOLDER
⑤ PROBE-STACK CONNECTOR
⑥ BRASS CLAMP
⑦ STAINLESS STEEL PROBE COVER
⑧
⑨ BRASS 3/4 PIPE TEE
3/4 ELEC 4" NIPPLE
⑩ COPPER COIL WITH ASBESTOS COVERED HEATING WIRE
⑪ PYREX CONDENSER
⑫ ELECTRICAL CONNECTOR LT
⑬ THREADED SWITCH
⑭ CONNECTOR CASE
⑮ ALUMINUM CHANNEL (CONDENSER - IMPINGER SUPPORT)

Figure 1-4. SO_x-NO_x Sampling Probe and Condenser.

was used to remove particulate matter. The stainless steel probe attached to the SO_x probe (Figure 1-4) was used to collect manual NO_x samples as well as CO_2 and O_2 for Orsat analysis. When the three trains (described in the following section and shown in Figure 1-5) were run in parallel, a glass tee wrapped with heating tape (controlled with a variac) was used to couple the trains to the probe. The samples *from all three trains* were collected simultaneously through the *same* probe in order to obtain comparisons of the three sampling methods. See Appendix A (Figure A-5).

1.3.2 Sampling Trains

The sampling procedures are described in detail in Appendix A. Schematics of the sampling trains used for the tests are shown in Figure 1-5. The trains are similar in that SO_2 is collected in midget impingers by absorption in aqueous hydrogen peroxide solution. The major difference between the trains was in the collection of SO_3. In train a, SO_3 was collected by filtration of the H_2SO_4 mist after the flue gas was cooled to a temperature between 60 and 90°C. This temperature is *below* the acid dewpoint and *above* the water dewpoint. The condenser is shown in Figure 1-6 and in detail in Figure 1-4. This controlled condensation collection procedure should lead to increased precision and/or accuracy of SO_3 determinations since the problem of oxidation of dissolved SO_2 is eliminated. In train b, SO_3 was collected in midget impingers by absorption in a mixture of 80% isopropanol (IPA) and 20% water. *Any residual SO_2 which remains in the IPA (train b) impingers after collection of a sample of flue gas was removed by flushing with an equal volume of clean air.* In train c, SO_3 was collected (and not determined) by absorption in a bubbler containing 80% isopropanol and 20% water. Any H_2SO_4 not removed in the isopropanol solution was collected on a glass wool plug following the bubbler. *Train c was not flushed with air since we wanted to determine the extent of loss of dissolved SO_2 in the IPA impinger.* The SO_2 results for this train were expected to be lower than trains a or b.

The metering systems for trains a and b are critical orifices while train c utilizes a dry test (integrating) meter. The a and b metering system is shown pictorially in Figure 1-7. In the first two trains,

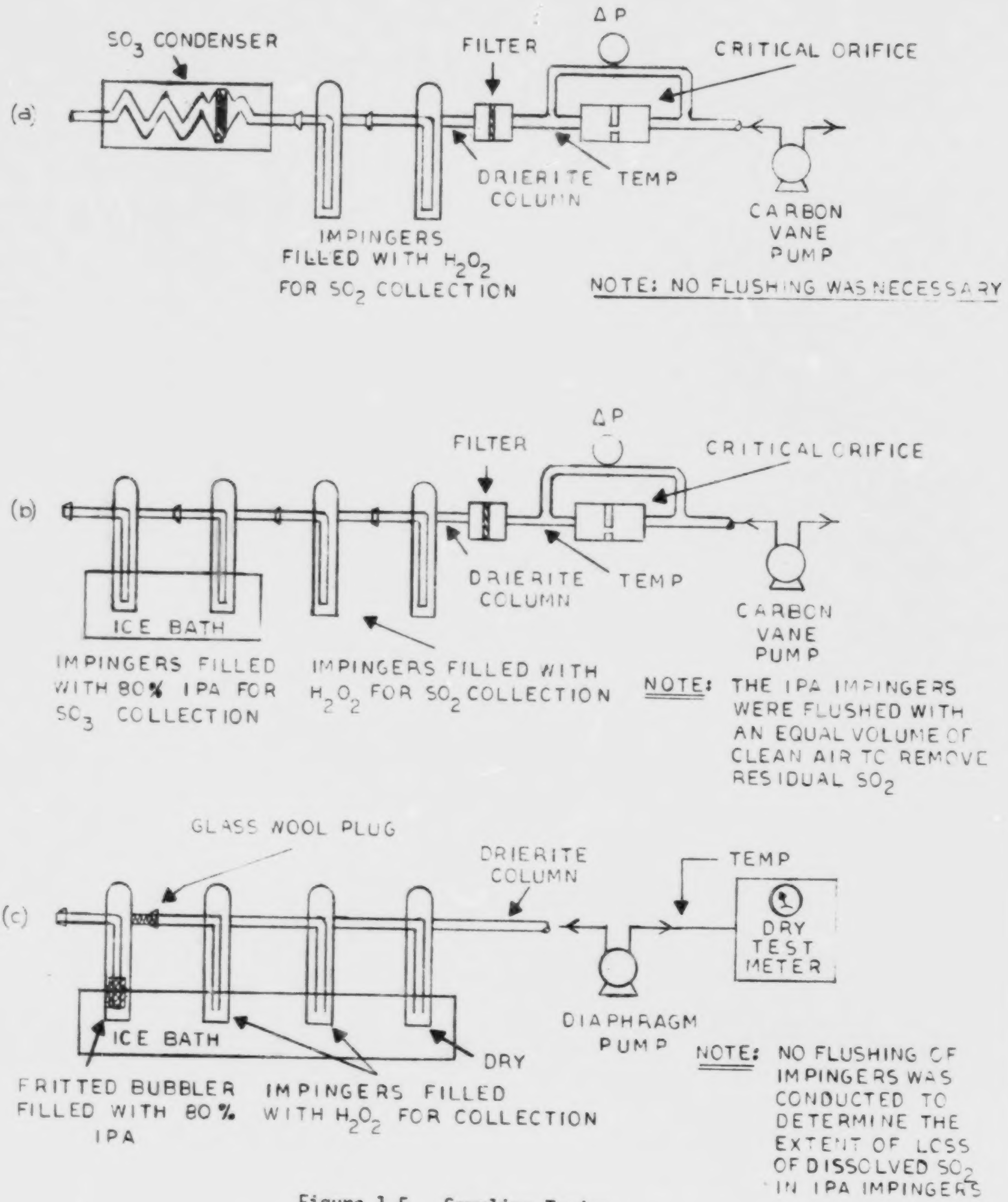

(a)
SO3 CONDENSER
FILTER
ΔP
CRITICAL ORIFICE
DRIERITE COLUMN
TEMP
CARBON VANE PUMP
IMPINGERS FILLED WITH H2O2 FOR SO2 COLLECTION
NOTE: NO FLUSHING WAS NECESSARY
(b)
FILTER
ΔP
CRITICAL ORIFICE
ICE BATH
DRIERITE COLUMN
TEMP
CARBON VANE PUMP
IMPINGERS FILLED WITH 80% IPA FOR SO3 COLLECTION
IMPINGERS FILLED WITH H2O2 FOR SO2 COLLECTION
NOTE: THE IPA IMPINGERS WERE FLUSHED WITH AN EQUAL VOLUME OF CLEAN AIR TO REMOVE RESIDUAL SO2
(c)
GLASS WOOL PLUG
DRIERITE COLUMN
TEMP
DRY TEST METER
ICE BATH
DIAPHRAGM PUMP
DRY
FRITTED BUBBLER FILLED WITH 80% IPA
IMPINGERS FILLED WITH H2O2 FOR COLLECTION
NOTE: NO FLUSHING OF IMPINGERS WAS CONDUCTED TO DETERMINE THE EXTENT OF LOSS OF DISSOLVED SO2 IN IPA IMPINGERS

Figure 1-5. Sampling Trains.

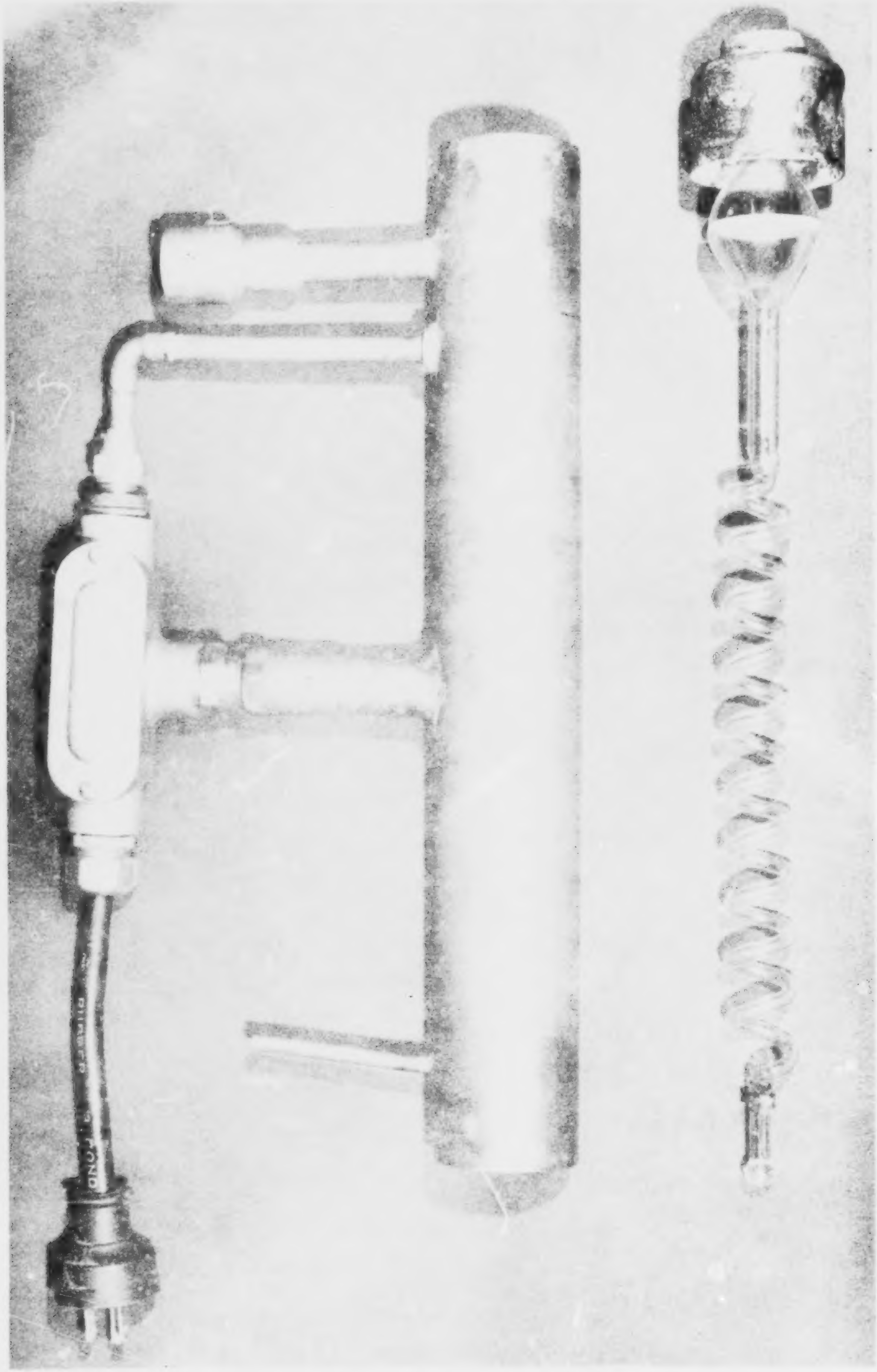


Figure 1-6. Controlled Condensation Collector for SO_3.

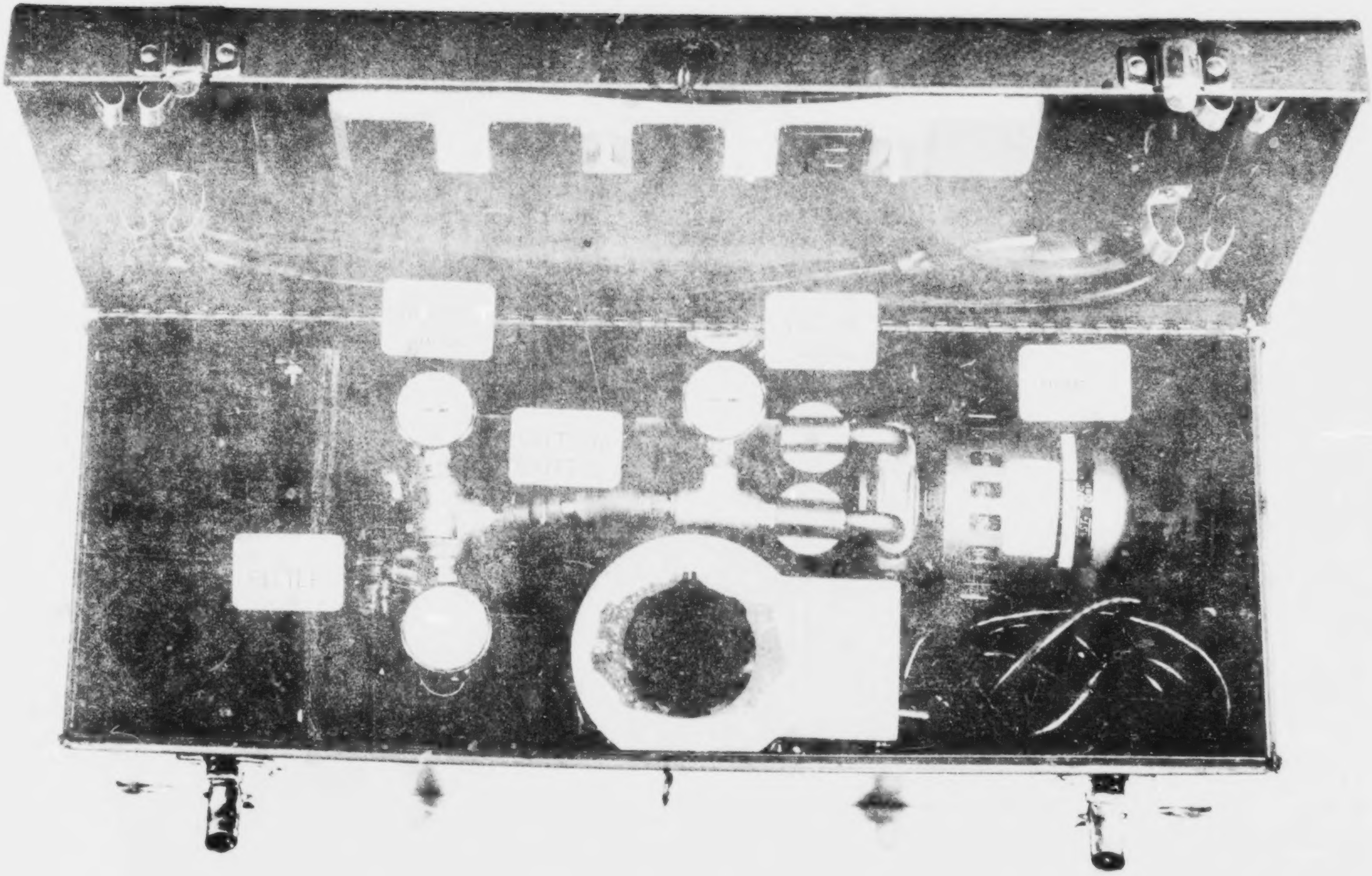


Figure 1-7. Walden Prototype Sampling System.

the time has to be accurately measured since the total volume of air metered is determined from the product of the sampling rate and the time. In order to eliminate any differences between the trains caused by the metering systems, all metering systems were checked with a spirometer initially and at frequent intervals (every two to four weeks) with a calibrated dry test meter. The results are discussed in the following section.

1.3.3 Calibration of Metering Devices and Variation with Time

The only "primary standards" for metering flow are the wet test meter and the spirometer. These devices are laboratory instruments and are *not* readily applicable for field use. Therefore, dry test meters and other portable metering equipment are used for field applications. These devices, however, *must* be calibrated since they are not "primary standards." We have calibrated the metering devices, used for the field tests, with a spirometer. A "new" dry test meter calibrated with the spirometer was kept in the laboratory for calibration purposes. This device was used to check the flow rates of all the orifices and dry test meters on a regular basis. The use of the secondary standard (dry test meter) was necessary because of the large number of calibrations required and the awkwardness of the spirometer. Thirty-four *different* Millipore critical orifices were checked with the dry test meter. Each result represents an average of three to five individual runs. The data are given in Table 1-6. Although many of these orifices are close to the rated values, errors as large as 50%, 15% and 10% were found for 0.5, 1.0 and 3.0 liter/min orifices. Note that smaller errors are found for the larger orifices. *Thus, these orifices must be calibrated prior to use.* A number of orifices were checked at regular intervals during the test program. The data are given in Table 1-7. No changes in calibration were observed although these orifices were used to collect as many as 20 to 50 field samples between calibrations.

1.3.4 Analytical Methods

The analytical methods used in this study include titration with with Ba^{++} ion (thorin indicator), or NaOH (bromphenol blue indicator) and colorimetric determination via barium chloranilate. The methods are described in detail in Appendix A and are briefly summarized in Figure 1-8.

TABLE 1-6

COMPARISON OF RATED AND MEASURED FLOW RATES FOR SOME MILLIPORE CRITICAL ORIFICES

Rated Value (l/min)	Measured Value (l/min)
0.5	0.54
	0.54
	0.27
	0.39
	0.50
	0.48
	0.45
	0.40
	0.46
	0.35
1.0	0.95
	1.01
	0.97
	1.01
	0.85
	1.09
	0.93
	1.04
	0.98
	1.04
	0.98
	1.01
	0.90
	1.03
3.0	3.08
	2.97
	3.11
	3.19
	2.84
	2.66
	2.79
	3.02
	2.84
	2.54

TABLE 1-7

VARIATION OF ORIFICE CALIBRATION WITH SAMPLING TIME IN THE FIELD*

Initial Flow Rate (l/min)	Recalibrated Flow Rate (l/min)	Total Sample Volume (l)
2.86	2.72	1800
2.66	2.63	1800
2.86	2.92	3800
2.78	2.81	3800
2.94	2.96	2700
3.04	3.07	2700
2.96	2.96	3000
2.86	2.85	3000
2.90	2.88	3000
0.52	0.49	3000

---

*The majority of this data was taken in the second phase of the program, e.g., at Category II sources (see following Section 2).

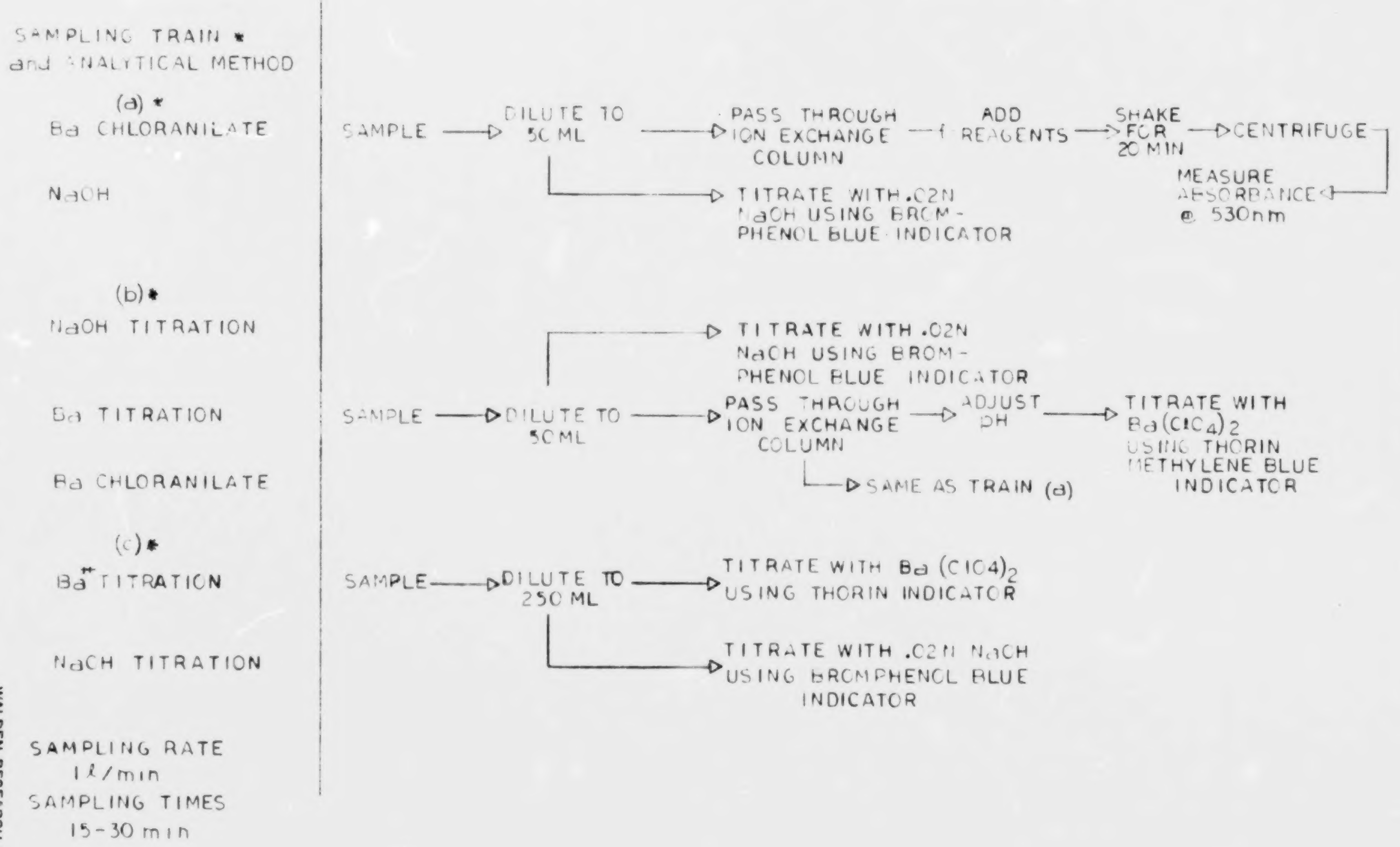

SAMPLING TRAIN *
and ANALYTICAL METHOD
(a) *
Ba CHLORANILATE
NaOH
(b)*
NaOH TITRATION
Ba TITRATION
Ba CHLORANILATE
(c)*
Ba⁺⁺ TITRATION
NaCH TITRATION
SAMPLING RATE
1 ℓ/min
SAMPLING TIMES
15-30 min
SAMPLE
DILUTE TO 5C ML
PASS THROUGH ION EXCHANGE COLUMN
ADD REAGENTS
SHAKE FOR 20 MIN
CENTRIFUGE
MEASURE ABSORBANCE @ 530nm
TITRATE WITH .C2N NaOH USING BROM-PHENOL BLUE INDICATOR
SAMPLE
DILUTE TO 5C ML
TITRATE WITH .02N NaCH USING BROM-PHENOL BLUE INDICATOR
PASS THROUGH ION EXCHANGE COLUMN
ADJUST pH
TITRATE WITH Ba(ClC4)2 USING THORIN METHYLENE BLUE INDICATOR
SAME AS TRAIN (a)
SAMPLE
DILUTE TO 250 ML
TITRATE WITH Ba (ClO4)2 USING THORIN INDICATOR
TITRATE WITH .C2N NaCH USING BRCMPHENCL BLUE INDICATOR

Figure 1-8. Flow Chart of Analytical Procedures.

Note in Figure 1-8 the samples for trains a and b were passed through a cation (Dowex resin) column to remove interference from metals present in the particulate matter. After the field test phase of the program was completed at fossil fuel-burning installations, we found poor agreement between measured and calculated results. The measured results were considerably lower than expected. Ba Chlor and Ba^{++} titration gave lower results on trains a and b than NaOH titration whereas in train c equivalent SO_2 results were obtained with Ba^{++} and NaOH titration. NaOH titration gave nearly the same SO_2 concentrations on all three trains. Since the major difference between the methods involved the treatment with the ion exchange resin, we began to suspect the recovery of sulfate from the resin. Therefore, we ran a comparison of a number of samples with and without the ion exchange step. The results are given in Table 1-8. The reduction in sulfate varies from 10 to 60% by either the barium ion titration or the barium chloranilate methods. Since the percent reduction varied widely with concentration, we ran some statistical analyses on the data to determine whether there was an effect of percent removal on concentration. The correlation coefficient was found to be 0.98 and the regression equation determined was $y = 168.2 + 1.08X$ (where X = with cation exchange). A plot of the data is shown in Figure 1-9.

Apparently the peroxide in the samples had some adverse effect on the cation exchange column. The peroxide causes the ion exchange column to swell. No swelling was encountered with synthetic H_2SO_4 samples which contained no peroxide. Unfortunately, all the a and b train samples by Ba^{++} and Ba Chlor were run using the cation exchange column. Therefore, we applied a correction to the measured data for these two methods in trains a and b using the regression equation of Figure 1-9. *All the a and b train data for SO_2 only by Ba^{++} and Ba Chlor on controlled coal, oil and uncontrolled coal have been corrected for the effect of the ion exchange resin. Any pilot plant data and samples in other industries were not affected since this problem was corrected prior to taking any samples there.*

A detailed write-up of all the procedures is given in Appendix A. *Note that the ion exchange step is not included.*

TABLE 1-8

EFFECT OF ION EXCHANGE STEP ON THE ANALYTICAL METHODS

ppm SO_2	
With Cation Exchange*	Without Cation Exchange*
Barium Chloranilate Analysis	
52	237
259	539
407	843
646	834
850	1128
940	1138
1137	1480
1229	1390
Barium Ion Titration	
260	519
256	326
150	314
193	344
160	270
131	296
218	308

---

*Run on aliquots of the same sample

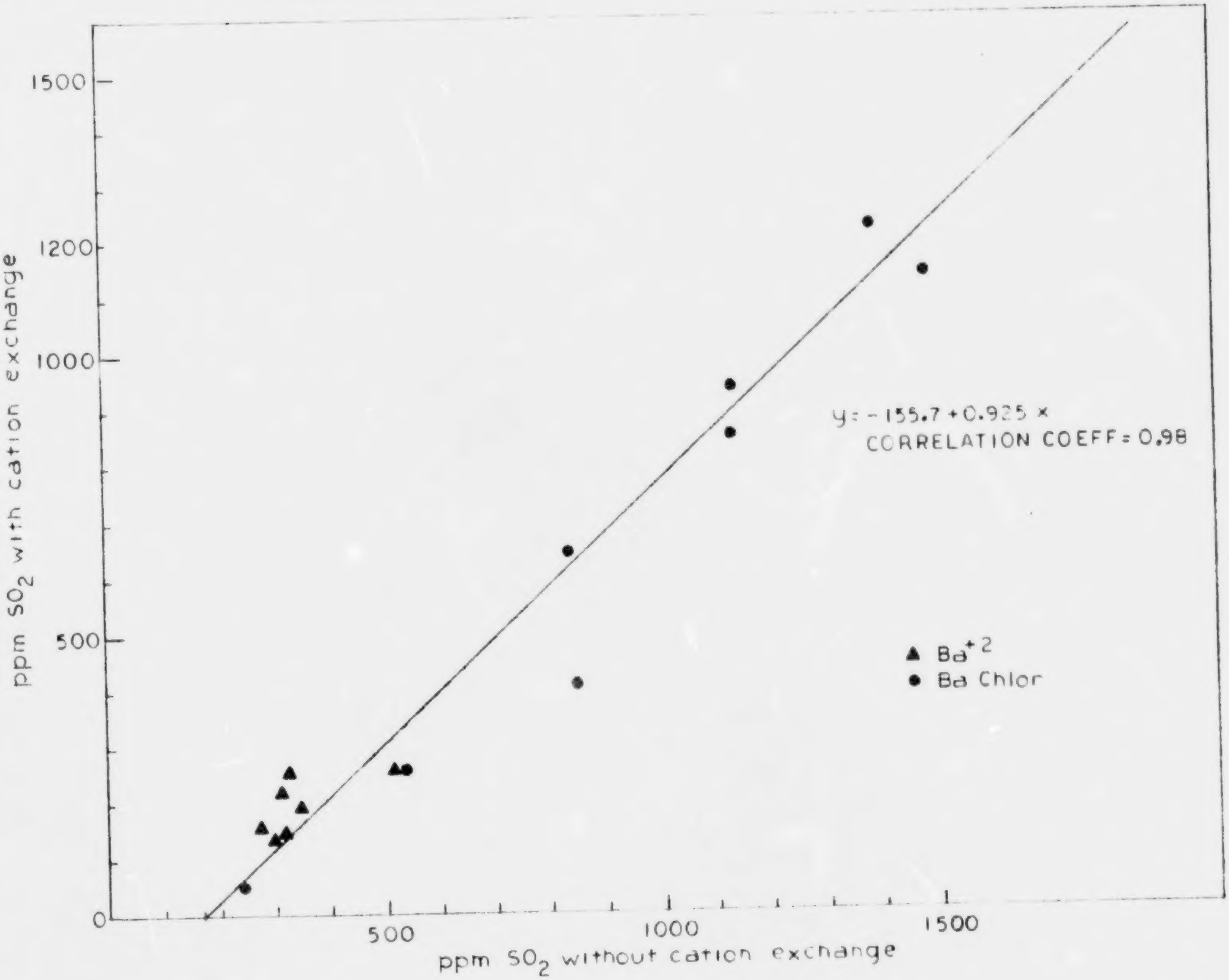


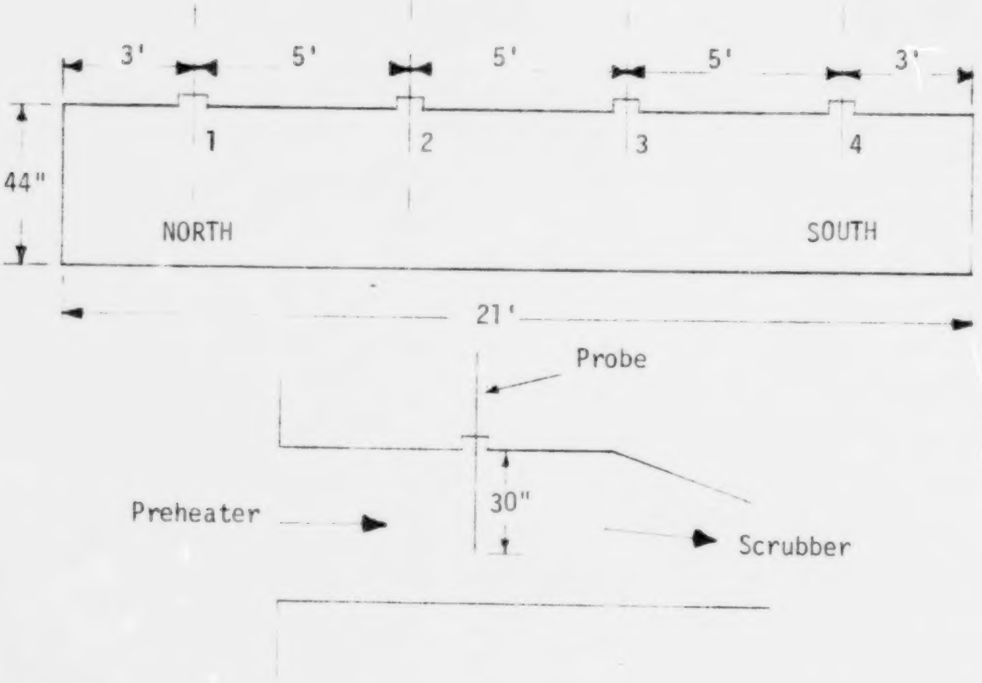
Figure 1-9. Effect of Cation Exchange Resin on the Removal of Sulfate.

1.4 SO_2 TEST RESULTS FOR A CONTROLLED COAL-FIRED POWER PLANT

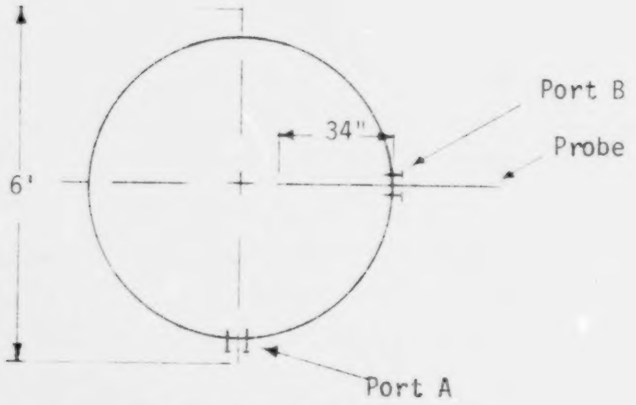
The test results described in this section were obtained at a coal-fired power plant equipped with a Combustion Engineering wet scrubbing system. The sampling port dimensions are given in Figure 1-10. This plant has a very high particulate loading at the scrubber inlet because of the injection of limestone for SO_x control. The resulting fly ash is basic and very reactive. The SO_2 test results obtained at the inlet to the scrubber are shown in Table 1-9. The SO_2 concentrations obtained in runs 5-10 were much lower than expected on the basis of the fuel analysis (Table 1-10). The calculated SO_2 concentration from the fuel analysis, assuming no conversion to $CaSO_4$, is about 2000 ppm. The measured values are only a fraction of this.

In later talks with Combustion Engineering, we found that they had encountered similar sampling problems. They were able to eliminate low SO_2 results by sampling at a low rate (0.25-0.5 liter/min) to minimize particulate buildup. Since we were running three SO_x trains off a single probe, our sampling rates (3-4 liters/min) were nearly an order of magnitude higher than those recommended by Combustion Engineering. The reaction of $CaCO_3$ with SO_2 could take place either in the probe (glass wool plug) or in the impingers. In the latter case, the NaOH titration would give much lower results than the barium ion titration because of the formation of $Ca(OH)_2$ and H_2CO_3 (by hydrolysis of $CaCO_3$) and subsequent reaction of $Ca(OH)_2$ with H_2SO_4. The barium chloranilate method would be unusable because of the complete precipitation of the acid chloranilate ion by Ca ion, a cationic interference. Neither of these effects seems to occur, therefore, the losses must be the result of reaction of SO_2 on the glass wool plug in the probe. Some recent experimental work by Galeano (1972) showed that a buildup of Na_2CO_3 on a glass wool "plug" in an SO_x sampling train reduced the recovery of SO_2. This tends to support our conclusions for this gas stream heavily laden with $CaCO_3$.

Some of the discrepancies between the trains (b and c) may be due to collection of some fly ash in the impingers. With train a (condenser), a


3'
5'
5'
5'
3'
44"
1
2
3
4
NORTH
SOUTH
21'
Probe
30"
Preheater
Scrubber

a. Inlet to Wet Scrubbing System.


Port B
34"
Probe
6'
Port A

b. Wet Scrubber Outlet.

Figure 1-10. Sampling Port Locations for Controlled Coal-Fired Power Plant.

TABLE 1-9

SO_2 TEST RESULTS FROM A CONTROLLED COAL-FIRED POWER PLANT AT THE INLET OF A WET SCRUBBER

Sample No.	Train a		Train b		Train c	
	ppm SO_2 (NaOH)	ppm SO_2 (Ba Chlor)	ppm SO_2 (NaOH)	ppm SO_2 (Ba^{++})	ppm SO_2 (NaOH)	ppm SO_2 (Ba^{++})
5A*	157	290	291	408	438	428
5B*	170	294	289	410	418	413
6A	13	184	1216	1094	272	313
6B	12	184	1214	1047	268	271
7A			305	459	287	332
7B			303	463	288	287
8A	134	234	126	276	150	148
8B	125	256	120	271	159	151
9A	132	253	120	271	137	149
9B	131	255	118	262	137	135
10A	34	192	101	238	85	103
10B	35	180	94	292	82	99

---

*A and B are aliquots of the same SO_2 sample.

TABLE 1-10

FUEL ANALYSIS FOR CONTROLLED COAL-FIRED POWER PLANT

Fuel	Component	%
Coal	S	3.72
		3.61
	C	76.39
		76.72
	H	4.36
		4.54
	N	0.93
		1.08

mechanical problem was encountered. The clamps attached to the condenser to seal this device to the impingers did not apply enough pressure to obtain an adequate seal. The condensers were modified in the field to eliminate this problem, and the runs after 10 show better agreement with the other trains.

Runs 11-20 (Table 1-11) were conducted at the *outlet of the wet scrubber* which was being run at about 50% SO_2 removal. The expected SO_2 concentrations at the scrubber outlet were ∿ 1000 ppm. The measured SO_2 values are in agreement with the stoichiometric concentrations. A major portion of the particulate (about 90%) is removed by the Combustion Engineering wet scrubbing system, thus, the problem encountered at the inlet would not be expected here.

No statistical results were calculated for the data in Table 1-9 (inlet).

A measure of the precision of an analytical method may be obtained by calculating the standard deviation from replicate measurements. The SO_2 determinations in Table 1-11 were run in duplicate. Since the mean is varying, the standard deviation must be calculated by the following equation:

$$ss = \sum_{i=1}^{t} [(Y_{1i} - \overline{Y}_i)^2 + (Y_{2i} - \overline{Y}_i)^2]$$

where ss is within runs sum of squares

t is the number of runs

Y_{1i} and Y_{2i} are the results of the duplicate analyses for the ith run

$\overline{Y}_i = \frac{Y_{1i} + Y_{2i}}{2}$ is the mean of the ith run

Since the mean is not constant and is calculated for each run, the total number of degrees of freedom in this sum of squares is equal to the number of runs. Hence, the variance within runs is:

TABLE 1-11

SO_2 TEST RESULTS FROM A CONTROLLED COAL-FIRED POWER PLANT AT THE OUTLET OF A WET SCRUBBER

Sample No.	Train a		Train b			Train c	
	ppm SO_2 (NaOH)	ppm SO_2 (Ba Chlor)	ppm SO_2 (NaOH)	ppm SO_2 (Ba^{++})	ppm SO_2 (Ba Chlor)	ppm SO_2 (NaOH)	ppm SO_2 (Ba^{++})
11A*	936	863	562	606		528	616
11B*	906	944	551	592		530	609
12A	471	565	602	596	604	514	571
12B	475	597	589	617	612	528	553
13A	528	577	612	637	629	548	608
13B	527	631	598	639	636	526	592
14A	685	740	750	755	787	684	741
14B	697	759	729	746	786	677	735
15A	555	653	706	636	692	667	694
15B	557	658	688	638	725	655	676
16A	1054	1004	737	729	828	490	542
16B	1063	1021	708	729	804	501	517
17A			566	632	707	535	562
17B			546	618	566	533	626
18A			505	529	469	518	563
18B			504	531	466	505	544
19A			449	502	504	354	411
19B			444	515	563	367	404
20A			441	489	503	435	494
20B			445	484	501	449	497

---

*A and B are aliquots of the same SO_2 sample.

$$\text{variance} = \sqrt{\frac{ss}{t}}$$

This value provides an unbiased estimate of the standard deviation and hence is a measure of the precision of the analytical method. The data calculated using the above equation is summarized in Table 1-12. The barium ion and NaOH titration procedures yield a precision of 1-2% which is typical at these SO_2 concentrations when no interferences are present. The precision of the barium chloranilate method is quite poor, about 5%, indicating the presence of an interference with the method. McCrone (1971) found that the particulate matter from this scrubber (for samples collected at the same time) was predominantly fine particles of $CaSO_4$. Since calcium is known to be an interference with the barium chloranilate method, this may account for the poorer precision of the method for this source.

Regression analysis and correlation coefficients were computed with a Compucorp 145E programmable calculator. The statistical intercomparison of the methods is given in Table 1-13. There appears to be better agreement between *different* methods on the *same* train than between the same analytical method on trains a, b or c. For example, Ba^{++} titration for train c vs b yields a poor correlation coefficient (0.67) whereas the NaOH titration vs Ba^{++} in either trains b or c gives correlation coefficients of 0.94 and 0.97, respectively. The SO_2 results for train c are lower than for either trains a or b. This is due to the lack of flushing to remove residual SO_2 from the 80% IPA absorber. *The SO_2 must be flushed from the IPA absorber following the test.* The mean SO_2 concentration by NaOH titration for runs 11-16 is more than 100 ppm lower for train c than for either train a or b.

We also see that the NaOH titration for train b vs c gives a lower correlation coefficient and poor regression equation, again the result of residual SO_2 left in the IPA scrubber for train c.

The Ba^{++} titration vs NaOH or Ba Chlor on train b yields essentially similar statistical results. Since methods specific for sulfate or hydrogen ion give the same results within any particular train, the differences between the trains may be the result of sampling rather than the analytical methods.

TABLE 1-12

PRECISION OF DUPLICATE ANALYSIS* OF SO_2 FOR A CONTROLLED COAL-FIRED POWER PLANT

Analytical Method	Sampling Train	No. of Samples	Mean SO_2 Concentration (ppm)	Standard Deviation (ppm)	CV (%)
Ba Chloranilate	(a)	11	515	23.2	4.5
	(b)	9	632	37.4	5.9
Ba^{++} Titration	(b)	16	553	6.3	1.1
	(c)	10	409	6.8	1.7
NaOH Titration	(a)	4	561	4.5	0.8
	(b)	6	653	13.2	2.0
	(c)	6	525	9.1	1.7

---

*Sampling errors not included (replicate analysis)

(a) SO_3 collected by condenser

(b) SO_3 collected in impinger containing 80% IPA

(c) SO_3 collected in bubbler containing 80% IPA

(b), (c): In all cases SO_2 is collected in H_2O_2

TABLE 1-13

REGRESSION ANALYSES AND CORRELATION COEFFICIENTS FOR A CONTROLLED COAL-FIRED POWER PLANT*

[illegible]thods Compared	Sample Size	Correlation Coefficient	Regression Equation
Ba^{++} Titration (c) [x] and Ba^{++} Titration (b) [y]	20	0.669	y = 0.619 x +253
Ba^{++} Titration (c) [x] and NaOH Titration (c) [y]	20	0.972	y = 0.964 x -29.8
Ba^{++} Titration (b) [x] and Ba Chloranilate (b) [y]	18	0.935	y = 1.27 x -143
Ba^{++} Titration (b) [x] and NaOH Titration (b) [y]	20	0.947	y = 1.17 x -128
Ba Chloranilate (b) [x] and Ba Chloranilate (a) [y]	10	0.871	y = 1.67 x -464
NaOH Titration (c) [x] and NaOH Titration (b) [y]	20	0.784	y = 0.903 x +110

---

*Outlet only

(a) Sampling train - condenser - two impingers

(b) Sampling train - four impingers

(c) Sampling train - bubbler - two impingers

For train a, we have a rather limited number of results for comparison and for train c, the incomplete removal of SO_2 from the IPA gives low SO_2 results. Hence, the apparent poor agreement between trains.

1.5 SO_2 RESULTS FOR AN OIL-FIRED POWER PLANT

A detailed layout of the 30 MW oil-fired power plant is shown in Figure 1-11. The sampling port schematic which shows the probe position in the duct following the electrostatic precipitator is given in Figure 1-12. The test results obtained at the oil-fired power plant are given in Table 1-14. These samples were collected with the sampling trains shown in Figure 1-5. The samples 29a and 29b in Table 1-14 were collected at the same time in two parallel probes. We found in later tests that the b system had a cracked probe. This accounted for the lower results obtained with probe b.

The precision of the analytical methods is excellent as seen in Table 1-15. The values for the coefficients of variation range from about 1.5 to 3%. The precision of titration methods seems to be slightly better than the barium chloranilate colorimetric method, however, all methods are in the CV range expected when interferences are minimal.

The statistical analysis of the data from Table 1-14 is tabulated in Table 1-16. The agreement between the methods is considerably better within a train [Ba^{++} titration (b) and barium chloranilate (b), Ba^{++} titration (c) and barium chloranilate (c), Ba^{++} titration (c) and NaOH titration (c)] than for comparing the same methods on different trains [Ba Chlor (a) and Ba Chlor (b), Ba^{++} titration (b) and Ba^{++} titration (c)]. The one exception to this is the NaOH titration (b and c). Excellent agreement is obtained since the NaOH titration aliquots *were not run through an ion exchange column*. The sulfate methods on trains a and b *but not c* were run through an ion exchange column. As noted in Section 1.3, the peroxide causes the resin to swell and take up some sulfate. The correction (see Figure 1-9) was applied to the sulfate methods (Ba^{++} and Ba Chlor) on trains a and b. Since the same correction was applied to the sulfate methods on train b, good agreement is obtained for Ba^{++} (b) and Ba Chlor (b).

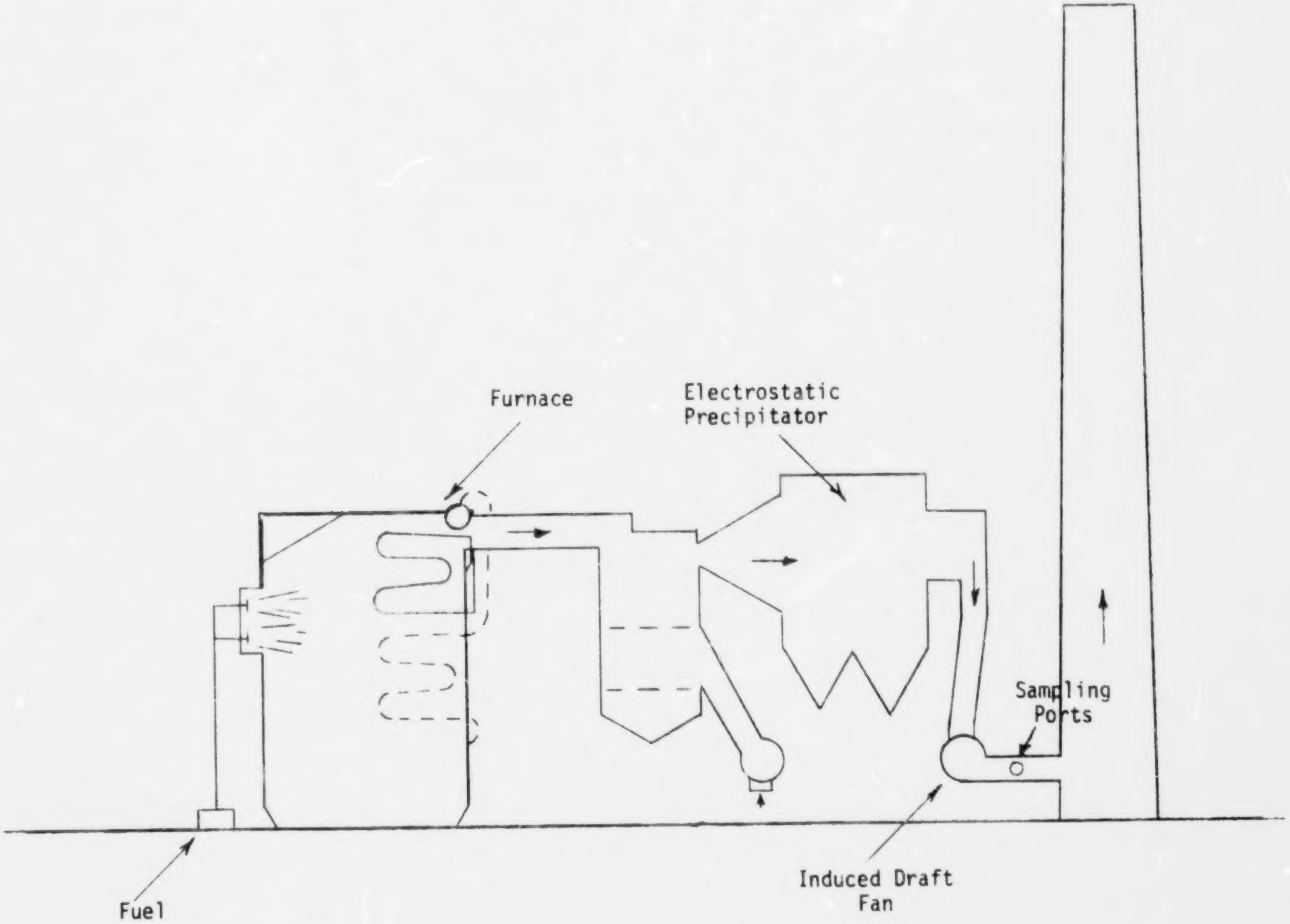

Furnace
Electrostatic Precipitator
Sampling Ports
Fuel
Induced Draft Fan

Figure 1-11. Schematic of the Oil-Fired Power Plant.

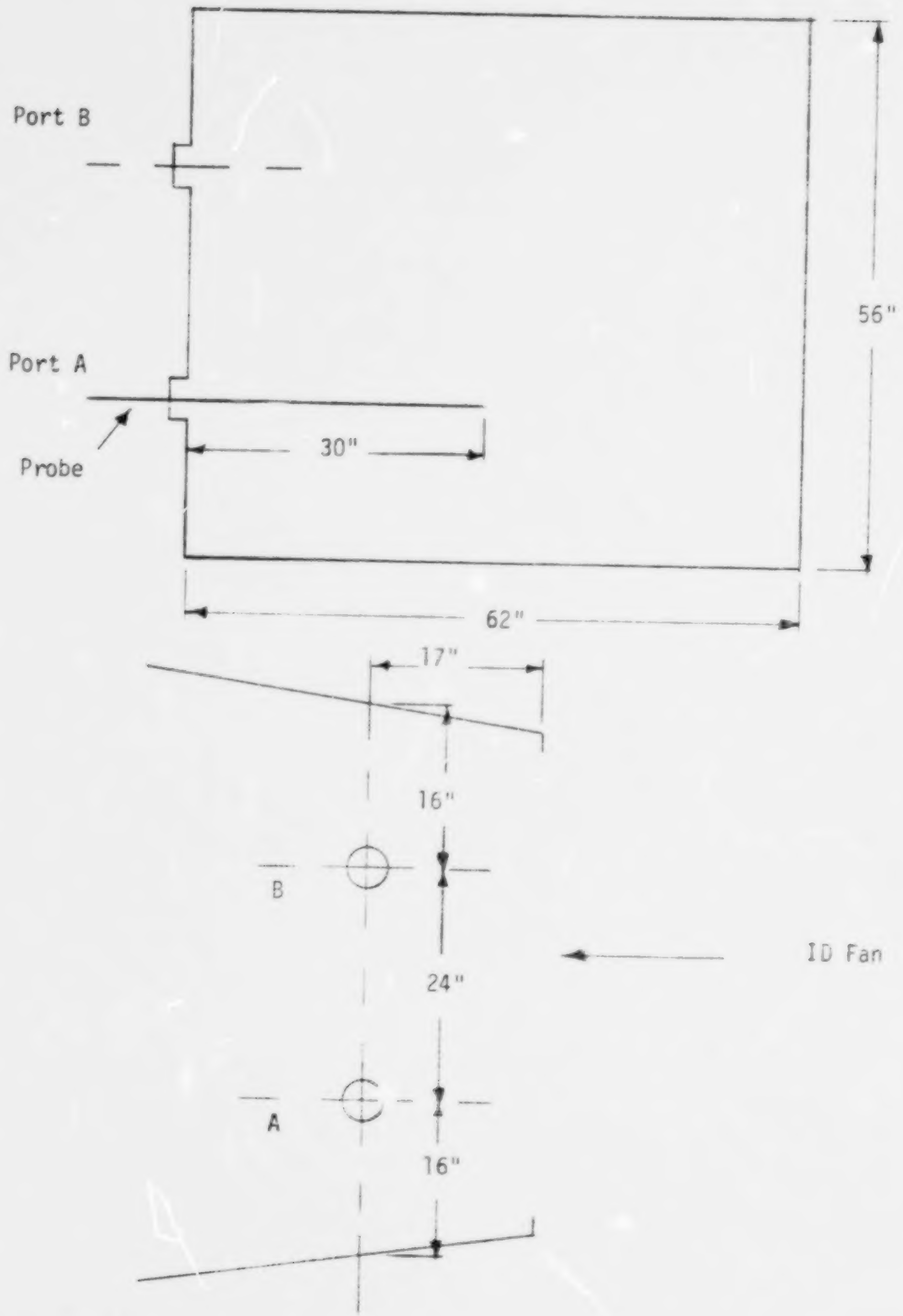

Port B
56"
Port A
Probe
30"
62"
17"
16"
B
ID Fan
24"
A
16"

Figure 1-12. Detail of Test Ports in an Oil-Fired Power Plant.

TABLE 1-14

SO_2 TEST RESULTS FROM AN OIL-FIRED POWER PLANT

Sample No.	Train a ppm SO_2 (NaOH)	ppm SO_2 (Ba Chlor)	Train b ppm SO_2 (NaOH)	ppm SO_2 (Ba^{++})	ppm SO_2 (Ba Chlor)	Train c ppm SO_2 (NaOH)	ppm SO_2 (Ba^{++})	ppm SO_2 (Ba Chlor)
1A†			251	432	396	259	269	225
1B†			256	434	401	259	261	385
3A			352	545	523	62	61	80
3B			348	550	523	63	60	125
4A			316	506	498	313	309	255
4B			311	505	469	319	314	315
21A	318	431	369	557	614	370	369	
21B	323	431	354	556	592	367	368	
22A	328	455	367	566	672	373	364	
22B	325	448	359	567	625	374	358	
23A	325	439	364	555	569	352	381	
23B	328	450	369	566	573	347	383	
24A	340	426	374	563	564	364	357	
24B	341	451	377	558	568	369	357	
25A	335	368	219	321	308	360	338	
25B	344	378	210	324	315	359	345	
27A	303	343	356	439	452	378	377	
27B	303	351	354	465	451	405	369	
28A	203	312	212	339	--	200	211	
28B	215	312	205	339	338	207	199	
29a-A			361	443	431	337	319	
29a-B			345	435	438	304	314	
29b-A			173	341	324	120	114	
29b-B			184	351	336	112	101	
30a-A			283	361	375	295	245	
30a-B			277	362	370	253	255	
30b-A			154	307	314	164	128	
30b-B			158	311	307	178	120	
31a-A			348	432	429	273	252	
31a-B			346	432	429	277	254	

TABLE 1-14 (continued)

Sample No.	Train a ppm SO_2 (NaOH)	ppm SO_2 (Ba Chlor)	Train b ppm SO_2 (NaOH)	ppm SO_2 (Ba^{++})	ppm SO_2 (Ba Chlor)	Train c ppm SO_2 (NaOH)	ppm SO_2 (Ba^{++})	ppm SO_2 (Ba^{++})
31b-A			220	336	322	143	130	
31b-B			204	336	325	154	137	
32a-A			306	410	393	298	276	
32a-B			309	403	396	296	282	
32b-A			169	327		106	85	
32b-B			164	339	396	95	83	
33a-A	209	309						
33a-B	211	312						
34A	311	363						
34B	323	338						
35A	280	356						
35B	281	332						
51A	320	403	376	445	451	373	346	352*
51B	327	394	380	449	446	400	345	368*
52A	264	383	295	390	393	211	214	233*
52B	276	369	298	392	372	213	217	222*
53A	275	350	304	391	377	350	355	356*
53B	280	371	316	394	395	357	354	362*
54A	311	378	335	412	393	301	295	293*
54B	303	375	332	410	397	299	295	299*
55A	289	341	319	307	271	284	279	287*
55B	288	344	320	313		300	280	281*
56A	295	368	314	401	378	302	287	284*
56B	292	383	318	407		304	285	288*

---

*These samples are titrated with barium perchlorate using the thorin-methylene blue mixed indicator.

†A and B are aliquots of the same SO_2 sample.

TABLE 1-15

PRECISION OF DUPLICATE SO_2 ANALYSIS* FOR AN OIL-FIRED POWER PLANT

Analytical Method	Sampling Train	No. of Samples	Mean SO_2 Concentration (ppm)	Standard Deviation (ppm)	CV (%)
Ba Chloranilate	(a)	19	367	10.7	2.9
	(b)	16	447	11.1	2.5
Ba^{++} Titration	(b)	18	444	5.9	1.4
	(c)	11	316	6.0	1.9
NaOH Titration	(a)	7	257	5.8	2.3
	(b)	15	282	6.3	2.2
	(c)	12	274	5.1	1.9

---

*Sampling errors not included (replicate analysis)

(a) SO_3 collected by condenser

(b) SO_3 collected in impingers containing 80% IPA

(c) SO_3 collected in a bubbler containing 80% IPA

SO_2 collected in H_2O_2 in all trains

TABLE 1-16

REGRESSION ANALYSES AND CORRELATION COEFFICIENTS FOR AN OIL-FIRED POWER PLANT

Methods Compared	Sample Size	Correlation Coefficient	Regression Equation
Ba^{++} Titration (b) [x] and Ba^{++} Titration (c) [y]	28	0.769	$y = 0.745\ x - 44.7$
Ba^{++} Titration (b) [x] and Ba Chloranilate (b) [y]	30	0.966	$y = 1.12\ x - 51.8$
Ba^{++} Titration (b) [x] and NaOH Titration (b) [y]	30	0.866	$y = 0.702\ x - 15.9$
Ba^{++} Titration (c) [x] and Ba Chloranilate (c) [y]	6	0.834	$y = 0.799\ x + 61.2$
Ba^{++} Titration (c) [x] and NaOH Titration (c) [y]	30	0.981	$y = 0.949\ x + 22.4$
Ba Chloranilate (a) [x] and NaOH Titration (a) [y]	14	0.752	$y = 0.623\ x + 60.4$
Ba Chloranilate (a) [x] and Ba Chloranilate (b) [y]	14	0.846	$y = 2.15\ x - 361$
NaOH Titration (b) [x] and NaOH Titration (c) [y]	28	0.930	$y = 1.03\ x - 18.2$

(a) Sampling train - condenser - two impingers

(b) Sampling train - four impingers

(c) Sampling train - bubbler - two impingers

With the NaOH titration (b) and (a) and barium titration (b) and barium chloranilate (a), lower correlations are obtained due to the correction of the sulfate methods. On the train c values which do not have to be corrected for the ion exchange absorption, good agreement is obtained for barium titration and NaOH titration.

The data indicate that although some differences are observed between the individual trains, *all the analytical methods* give reliable results.

The data on fuel composition and flue gas analysis are given in Tables 1-17 and 1-18, respectively, and were used to calculate the stoichiometric SO_2 values.

A comparison of the calculated and measured SO_2 values are given in Tables 1-19 through 1-21 for the barium chloranilate, barium ion titration and NaOH titration methods, respectively.

In Table 1-19, the train a results are 14% lower (on the average) than train b results. The fact that values > 100% are measured is probably due to the correction for sulfate adsorbed on the ion exchange resin. The large intercept for the data in Figure 1-9 tends to overemphasize values in the low concentration range.

Note that in Table 1-20, the train b results are > 100% of theoretical. This, again, may be due to the correction of the results (as above). Train c barium titration yields considerably lower results than train b, however, these % theoretical values are in good agreement with the NaOH values in trains a-c which were not subject to correction. Thus, the % theoretical values for the methods may be expected to be in the range of 80-90%.

1.6 SO_2 RESULTS FOR AN UNCONTROLLED COAL-FIRED POWER PLANT

SO_2 samples were collected at a coal-fired power plant which burned about 1% S fuel. The unit is essentially uncontrolled since the Aerotec cyclones have an efficiency of approximately 30%. The unit schematic and sampling port locations are shown in Figures 1-13 and 1-14, respectively. All the SO_2 samples were collected on the south side of the duct. The

TABLE 1-17

FUEL ANALYSIS FOR AN OIL-FIRED POWER PLANT

Fuel	Component	%	Date
Oil	S	0.98	3/20/71
		0.99	
		0.95	3/31/72
		0.94	
		0.95	4/1/72
		0.99	
		0.97	4/9/71
		0.94	
	C	85.33	3/30/71
		85.18	
	H	13.62	
		13.74	
	C	85.19	3/31/71
		86.62	
	H	13.85	3/31/72
		13.72	

TABLE 1-18

SUPPLEMENTARY FIELD TEST DATA FOR AN OIL-FIRED POWER PLANT

Date	Test No.	O_2 (%)	CO_2 (%)	T (°F)
3/18/71	1	7.0	8.5	310
	2	7.5	8.5	310
	3	6.8	8.5	310
	4	7.5	7.7	310
3/30/71	21	9.0	9.4	320
	22	8.6	10.0	320
	23	8.6	9.7	315
	24	8.7	9.0	320
3/31/71	25	8.7	9.0	320
	26	8.5	9.1	320
	27	8.5	9.1	315
	28	9.1	9.3	315
4/1/71	29	9.2	9.0	315
	30	8.3	9.5	315
	31	8.7	9.5	315
	32	9.0	9.5	315
	33	9.2	10.0	315
	34	8.0	9.6	315
4/2/71	35	9.1	9.0	315
	36	9.8	9.5	315
4/7/71	51		10.1	320
	52		8.5	320
	53	12.2	8.4	320
	54	10.7	8.7	320
	55	10.5	8.5	320
	56	11.1	8.1	320

TABLE 1-19

COMPARISON OF MEASURED AND CALCULATED SO_2 VALUES FOR AN OIL-FIRED POWER PLANT BARIUM CHLORANILATE METHOD

Sample No.	ppm SO_2 Theoretical	Train a		Train b	
		ppm SO_2	% Theor	ppm SO_2	% Theor
21	394	431	109	603	153
22	420	451	107	650	155
23	401	445	111	571	142
24	378	438	116	566	150
25	366	373	102	312	85
27	370	347	94	451	122
28	370	312	84	338	91
29a	378	311	83	435	115
30a	369	--	--	370	100
31a	390	--	--	429	110
32a	390	--	--	395	101
34	393	350	89	--	--
51	423	398	94	448	106
52	356	375	105	383	108
53	352	360	103	386	110
54	364	376	103	395	109
55	356	342	96	271	76
56	339	375	111	378	112
	Av. % Theoretical		100		114

TABLE 1-20

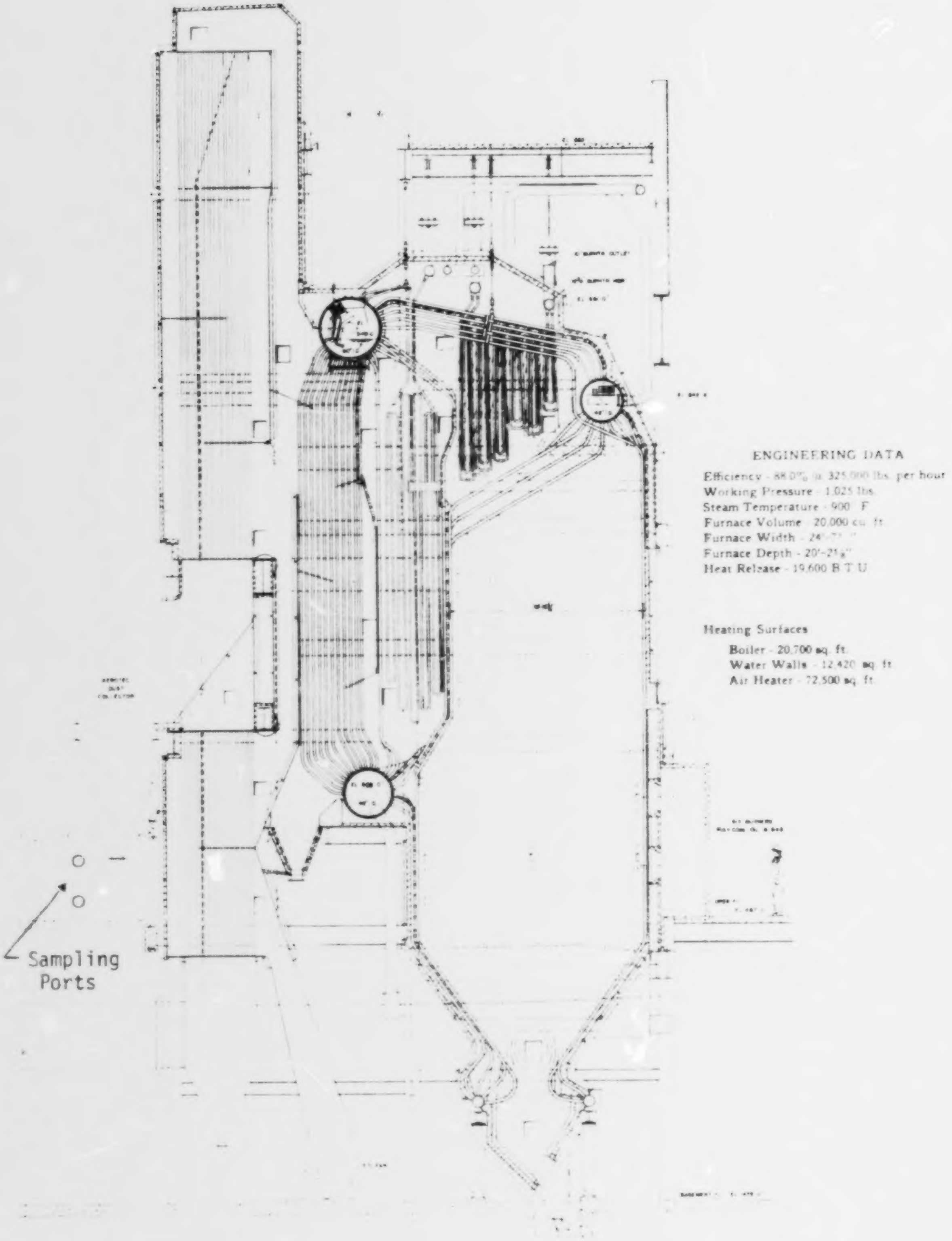
COMPARISON OF MEASURED AND CALCULATED SO_2 VALUES FOR AN OIL-FIRED POWER PLANT Ba^{++} TITRATION METHOD

Sample No.	ppm SO_2 Theoretical	Train b		Train c	
		ppm SO_2	% Theor	ppm SO_2	% Theor
21	394	556	141	369	94
22	420	566	135	361	86
23	401	560	140	382	95
24	378	560	148	357	94
25	366	322	88	342	93
27	370	452	122	373	100
28	370	339	92	205	55
29a	378	439	116	317	84
30a	369	362	98	250	68
31a	390	432	111	253	65
32a	390	406	104	279	72
34	393	--	--	--	--
51	423	448	106	346	82
52	356	391	110	216	61
53	352	392	111	355	100
54	364	411	113	295	81
55	356	410	115	280	79
56	339	404	119	286	84
	Av. % Theoretical		116		82

TABLE 1-21

COMPARISON OF MEASURED AND CALCULATED SO_2 VALUES FOR AN OIL-FIRED POWER PLANT NaOH TITRATION METHOD

Sample No.	ppm SO_2 Theoretical	Train a		Train b		Train c	
		ppm SO_2	% Theor	ppm SO_2	% Theor	ppm SO_2	% Theor
21	394	321	81	361	92	368	93
22	420	327	78	368	88	374	89
23	401	327	82	366	91	350	87
24	378	340	90	375	99	366	97
25	366	340	93	214	58	360	98
27	370	303	82	355	96	392	106
28	370	209	56	208	56	204	55
29a	378	--	--	353	93	320	85
30a	369	--	--	280	76	274	74
31a	390	--	--	347	89	275	71
32a	390	--	--	306	78	297	76
34	393	317	81	--	--	--	--
51	423	324	77	378	89	386	91
52	356	270	76	296	83	212	60
53	352	278	79	310	88	354	101
54	364	307	84	333	91	300	82
55	356	289	81	319	90	292	82
56	339	294	87	316	93	303	89
	Av. % Theoretical		81		85		84



ENGINEERING DATA

Efficiency - 88.0% @ 325,000 lbs. per hour
Working Pressure - 1,025 lbs.
Steam Temperature - 900° F
Furnace Volume - 20,000 cu. ft.
Furnace Width - 24'-7"
Furnace Depth - 20'-2⅛"
Heat Release - 19,600 B.T.U.

Heating Surfaces
  Boiler - 20,700 sq. ft.
  Water Walls - 12,420 sq. ft.
  Air Heater - 72,500 sq. ft.

Figure 1-13. Uncontrolled Coal-Fired Power Plant.

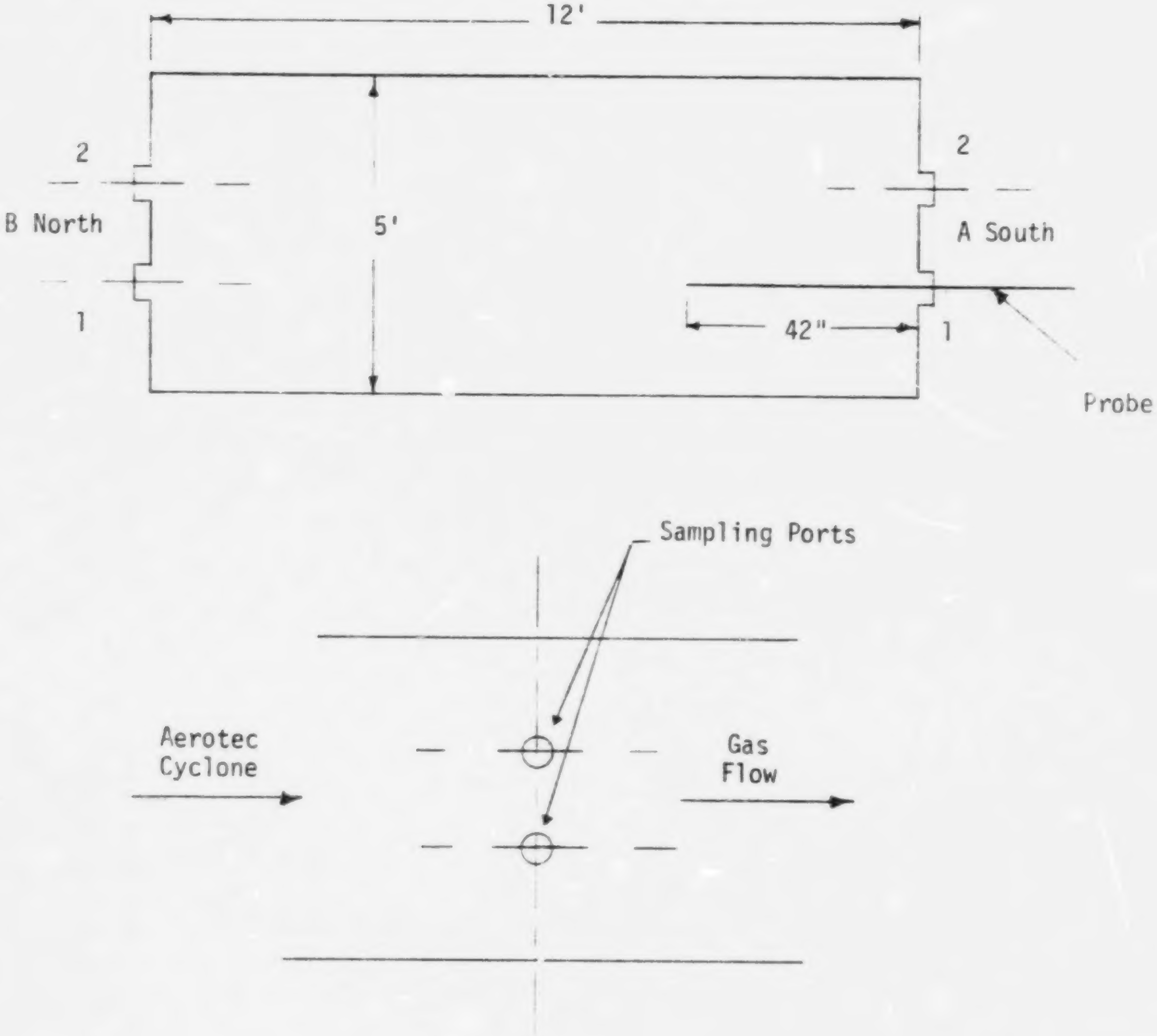

12'
2
2
B North
5'
A South
1
42"
1
Probe
Sampling Ports
Aerotec
Cyclone
Gas
Flow

Figure 1-14. Sampling Port Locations for the Uncontrolled Coal-Fired Power Plant.

other ports were welded onto the duct to allow a velocity profile to be determined.

The test data obtained by running three trains in parallel off the same probe are given in Table 1-22. The detail of each train is shown above in Figure 1-5. The analytical methods appear to give good agreement between trains except for Ba Chlor in train c (Table 1-22). Here the problem is a very dilute sample. In the analytical scheme in Figure 1-8, train c is diluted to 250 ml prior to aliquoting. This leads to a low absorbance and large error for the chloranilate method. The titration methods can compensate for the larger dilution by taking a larger aliquot for titration. This is difficult to do for the Ba Chlor colorimetric procedure.

The precision for replicate analysis of samples in Table 1-23 indicates no major interferences with the methods. Coefficients of variation between 1-3.5% are very similar to the results obtained at the oil-fired power plant (see Section 1.5). The precision appears to be about the same for each train, e.g., NaOH titration CV = 2 ± 1% for a, b, or c train, etc.

The regression analyses and correlation coefficients for the data in Table 1-22 have been calculated and are tabulated in Table 1-24. Again, Ba^{++} titration and Ba Chlor agree well within each train (a and b). The agreement for the Ba Chlor method on train c is poor compared to other analytical methods because of the dilution (see above). The NaOH titration comparisons to sulfate methods for train a and b has a large intercept because of the corrections applied to the sulfate methods (Section 1.3.3). The correlations between trains appear to be better on these samples than on either of the other sites tested. There is no apparent reason for this since interferences did not seem to be a problem on the oil-fired power plant results. The data in Table 1-24 indicates that each of the methods yields good results with no interferences for this coal-fired power plant.

Data on flue gas composition (CO_2, O_2) and fuel analysis are given in Tables 1-25 and 1-26. Stoichiometric SO_2 values were calculated as described in Section 1.5 and are compared with Ba Chlor, Ba^{++} titration, and NaOH titration in Tables 1-27 to 1-29.

TABLE 1-22

SO_2 TEST RESULTS FROM AN UNCONTROLLED COAL-FIRED POWER PLANT

Sample No.	Train a			Train b			Train c		
	ppm SO_2 (NaOH)	ppm SO_2 (Ba^{++})	ppm SO_2 (Ba Chlor)	ppm SO_2 (NaOH)	ppm SO_2 (Ba^{++})	ppm SO_2 (Ba Chlor)	ppm SO_2 (NaOH)	ppm SO_2 (Ba^{++})	ppm SO_2 (Ba Chlor)
37A*	494	513	--	528	968	536	865	989	369
37B*	506	--	--	513	973	556	880	1005	332
38A	437	446	443	467	470	465	397	395	264
38B	407	452	445	465	473	474	412	396	264
39A	416	463	443	425	484	448	405	363	254
39B	408	--	453	425	485	483	387	358	254
40A		426	--	411	461	411	392	315	168
40B	380	424	424	411	450	450	389	308	252
41A	335	424	410	408	465	410	388	334	215
41B	347	428	423	405	511	420	379	327	315
42A	0	--	--	324	408	396	152	148	146
42B	0	--	--	326	408	396	170	147	119
43A	340	411	380	335	408	396	294	292	264
43B	347	398	395	331	414	399	315	284	352
44A	422	453	443	398	423	404	420	292	0
44B	412	443	453	405	424	429	359	294	--
45A	405	483	464	410	465	447	294	376	223
45B	412	487	476	404	474	477	330	383	--
46A	372	436	431	313	443	431	346	342	176
46B	377	439	417	319	446	448	367	327	--
47A	328	414	418	335	422	410	312	256	189
47B	319	424	405	331	427	403	309	248	--
48A	470	485	475	467	502	502		455	363
48B	448	492	431	500	503	482	266	452	--
49A	481	525	538	499	517	539	429	407	351
49B	486	524	530	499	536	553	446	400	--
50A	503	519	530	500	505	490	582	596	496
50B	501	520	530	506	497	502	580	588	--

---

*Where A and B are aliquots of the same sample.

TABLE 1-23

PRECISION OF DUPLICATE SO_2 ANALYSIS* FOR AN UNCONTROLLED COAL-FIRED POWER PLANT

Analytical Method	Sampling Train	No. of Samples	Mean SO_2 Concentration (ppm)	Standard Deviation (ppm)	CV (%)
Ba Chloranilate	(a)	11	452	11.8	2.6
	(b)	14	456	14.6	3.2
Ba^{++} Titration	(a)	11	457	5.5	1.2
	(b)	11	457	4.8	1.0
	(c)	13	342	5.0	1.5
NaOH Titration	(a)	12	415	9.3	2.2
	(b)	14	416	7.4	1.8
	(c)	11	418	14.3	3.4

---

*Sampling errors not included (replicate analysis)

(a) SO_3 collected by condenser

(b) SO_3 collected in impingers containing 80% IPA

(c) SO_3 collected in a bubbler containing 80% IPA

SO_2 collected in H_2O_2 in all trains

TABLE 1-24

REGRESSION ANALYSES AND CORRELATION COEFFICIENTS FOR AN UNCONTROLLED COAL-FIRED POWER PLANT

Methods Compared	Sample Size	Correlation Coefficient	Regression Equation
Ba^{++} Titration (a) [x] and Ba Chloranilate (a) [y]	22	0.939	$y = 1.09\ x - 50.9$
Ba^{++} Titration (b) [x] and Ba Chloranilate (b) [y]	26	0.853	$y = 1.01\ x - 20.5$
Ba^{++} Titration (c) [x] and Ba Chloranilate (c) [y]	16	0.813	$y = 0.688\ x + 41.6$
Ba^{++} Titration (a) [x] and NaOH Titration (a) [y]	23	0.924	$y = 1.36\ x - 215$
Ba^{++} Titration (b) [x] and NaOH Titration (b) [y]	26	0.848	$y = 1.46\ x - 266$
Ba^{++} Titration (c) [x] and NaOH Titration (c) [y]	27	0.945	$y = 0.776\ x + 97.0$
Ba^{++} Titration (a) [x] and Ba^{++} Titration (b) [y]	23	0.788	$y = 0.731\ x + 132$
Ba^{++} Titration (a) [x] and Ba^{++} Titration (c) [y]	23	0.786	$y = 1.75\ x - 429$
Ba Chloranilate (a) [x] and Ba Chloranilate (b) [y]	23	0.859	$y = 0.849\ x + 72.5$
Ba Chloranilate (a) [x] and Ba Chloranilate (c) [y]	17	0.557	$y = 0.914\ x - 113$
NaOH Titration (a) [x] and NaOH Titration (b) [y]	25	0.885	$y = 1.01\ x + 5.75$
NaOH Titration (b) [x] and NaOH Titration (c) [y]	26	0.776	$y = 0.953\ x + 2.04$
NaOH Titration (a) [x] and NaOH Titration (c) [y]	23	0.820	$y = 1.13\ x - 62.9$
Ba Chloranilate (a) [x] and Ba^{++} Titration (b) [y]	23	0.730	$y = 0.597\ x + 198$

(a) Sampling train - condenser - two impingers
(b) Sampling train - four impingers
(c) Sampling train - bubbler - two impingers

TABLE 1-25

SUPPLEMENTARY FIELD TEST DATA FOR AN UNCONTROLLED COAL-FIRED POWER PLANT

Date	Test No.	Fuel	O_2 (%)	CO_2 (%)	T (°F)
4/5/71	37	Coal	9.0	12.0	350
			7.5	13.5	
4/6/71	38	Coal	5.8	14.7	350
	39	Coal	5.0	13.7	350
	40	Coal	4.6	14.5	350
	41	Coal	5.4	13.4	350
	42	Coal	5.5	13.8	350
	43	Coal	5.3	14.3	350
	44	Coal	5.3	14.1	350
4/7/71	45	Coal	6.7	13.4	345
	46	Coal	6.3	13.0	345
	47	Coal	6.5	12.1	345
	48	Coal	6.5	13.2	345
	49	Coal	6.5	13.2	345
	50	Coal	6.1	13.4	345

TABLE 1-26

FUEL ANALYSES FOR AN UNCONTROLLED COAL-FIRED POWER PLANT

Component	%	Date
S	0.79	4/5/71
	0.84	
	0.90	4/6/71
	0.86	
	1.05	4/7/71
	1.07	
C	76.39	
	76.72	
H	4.36	
	4.54	
N	0.93	
	1.08	

TABLE 1-27

COMPARISON OF MEASURED AND CALCULATED SO_2 VALUES FROM AN UNCONTROLLED COAL-FIRED POWER PLANT
BARIUM CHLORANILATE METHOD

Sample No.	ppm SO_2 Theoretical	Train a		Train b		Train c	
		ppm SO_2	% Theor	ppm SO_2	% Theor	ppm SO_2	% Theor
37	469	--	--	546	116	350	75
38	557	444	80	470	84	264	47
39	536	448	84	465	87	254	47
40	568	424	75	430	101	210	37
41	525	416	79	415	79	265	50
42	541	--	--	396	73	132	24
43	561	388	69	398	71	308	55
44	553	448	81	415	75	--	--
45	639	470	74	462	72	223	35
46	620	425	69	440	71	176	28
47	577	412	71	407	71	189	33
48	630	450	71	490	78	363	58
49	630	534	85	545	87	351	56
50	639	530	83	495	77	496	78
	Av. % Theoretical		77		82		48

TABLE 1-28

COMPARISON OF MEASURED AND CALCULATED SO_2 VALUES FROM
AN UNCONTROLLED COAL-FIRED POWER PLANT
Ba^{++} TITRATION METHOD

Sample No.	ppm SO_2 Theoretical	Train a		Train b		Train c	
		ppm SO_2	% Theor	ppm SO_2	% Theor	ppm SO_2	% Theor
37	469	513	109	--	--	--	--
38	557	449	81	472	85	395	71
39	536	463	86	485	90	360	67
40	568	425	75	455	80	312	55
41	525	426	81	488	93	330	63
42	541	--	--	408	75	147	27
43	561	405	72	418	75	288	51
44	553	448	81	445	80	293	53
45	639	485	76	460	72	380	59
46	620	437	70	445	72	335	54
47	577	419	73	425	74	252	44
48	630	488	77	503	80	453	72
49	630	525	83	526	83	403	64
50	639	520	81	500	78	592	93
	Average Theoretical		80		80		59

TABLE 1-29

COMPARISON OF MEASURED AND CALCULATED SO_2 VALUES FROM AN UNCONTROLLED COAL-FIRED POWER PLANT
NaOH TITRATION METHOD

Sample No.	ppm SO_2 Theoretical	Train a		Train b		Train c	
		ppm SO_2	% Theor	ppm SO_2	% Theor	ppm SO_2	% Theor
37	469	500	107	520	111	--	--
38	557	422	76	466	84	405	73
39	536	412	77	425	79	395	74
40	568	380	67	411	72	390	69
41	525	340	65	40[illegible]	77	383	73
42	541	--	--	325	60	160	30
43	561	343	61	333	59	305	54
44	553	417	75	373	67	390	71
45	639	410	64	407	64	315	49
46	620	375	60	316	51	355	57
47	577	324	56	333	58	310	54
48	630	460	73	480	76	266	42
49	630	483	77	499	79	437	69
50	639	502	79	503	79	581	91
	Av. % Theoretical		72		73		62

The Ba Chlor method yields results which are about 80% of the theoretical concentration for trains a and b. The results for Ba Chlor in train c should be disregarded since the sampling procedure required dilution to 250 ml before an aliquot was taken. This led to a very low absorbance and, therefore, poor accuracy since a small absorbance had to be multiplied by a large dilution factor. The Ba^{++} titration results for trains a and b indicate about 80% of theoretical which is the same as that for Ba Chlor. Train c was not flushed to remove residual SO_2 from the IPA absorber (see Figure 1-8). This can account for the low results since SO_2 is soluble in the water-alcohol mixture.

The NaOH titration results for trains a and b (Table 1-24) are slightly lower than the sulfate methods. It is not clear whether this is real or an artifact of the adjustment of the sulfate methods. Again, train c produces lower SO_2 results because the residual SO_2 was not removed (by flushing) from the IPA absorber.

1.7 SO_3 RESULTS FROM FOSSIL FUEL COMBUSTION SOURCES

The major problem in quantitative collection of SO_3 in power plant effluents is that SO_2, present in a large excess, is easily oxidized, leading to high SO_3 values and/or poor precision and accuracy. Most collection methods for the sulfur oxides have been based upon physical separation of SO_2 and SO_3 (by differential absorption) to reduce the magnitude of the oxidation problem. Techniques in which both oxides are collected without separation (such as absorption in caustic solution) have not been widely used since accuracy is generally poor due to oxidation of dissolved SO_2.

SO_3 collection techniques may be divided by approach into two different classes: absorption and condensation methods. The former depends on the solubility of H_2SO_4 in aqueous solutions. Inhibitors, such as alcohols, have generally been added to prevent the oxidation of dissolved SO_2. Junge and Ryan (1958) have found that trace metals catalyze the oxidation of SO_2 to sulfate. It is very difficult to inhibit the oxidation of SO_2 in solution, therefore, the absorption method may lead to poor accuracy. The condensation method depends upon controlled cooling of the flue gas to a temperature where H_2SO_4 aerosol is formed and subsequent collection on a sintered glass frit or filter paper. The important feature of the controlled condensation method is that the temperature of the *collector is maintained* at 60-90°C which is *above the typical water dewpoint (40-45°C) for combustion sources.* This eliminates the problem of SO_2 dissolving in an aqueous phase and being oxidized to $SO_4^=$.

The controlled condensation method should lead to improved accuracy in SO_3 determinations. In order to assess these methods, IPA and controlled condensation trains were run at each of the sources. The trains are shown schematically in Figure 1-5 and the condenser in detail in Figures 1-4 and 1-6.

The results obtained for SO_3 determinations are given in Table 1-30. The ion exchange step was eliminated in the procedure to prevent losses of sulfate observed previously for the barium ion titration. The controlled condensation method (analyzed by Ba Chlor) gives considerably higher results for the oil-fired plant than the 80% IPA absorption (analyzed by Ba^{++} titration). The average SO_3 concentration results found for the controlled condensation method at the coal-fired power plant with the Combustion Engineering wet scrubbing system is about the same as IPA absorption but the correlation coefficient for the results is only 0.1. At the uncontrolled coal-fired plant, lower results were observed for the controlled condensation method. The 80% IPA results obtained for the oil-fired plant give an SO_3 concentration which is about 40% of that obtained by the controlled condensation method. For the controlled coal-fired plant, the IPA results are about 70% of the values obtained by the controlled condensation technique. In the uncontrolled coal-fired plant, however, the situation is reversed. The controlled condensation technique yields a mean SO_3 concentration which is about 2/3 of the 80% IPA value. The correlation coefficient for the SO_3 tests for the oil-fired power plant is 0.4 and about zero for the uncontrolled coal-fired power plant. The large difference between the SO_3 methods is quite alarming and should be investigated in detail.

TABLE I-30

SO_3 TEST RESULTS FOR FOSSIL FUEL COMBUSTION

Sample No.	Controlled Condensation ppm SO_3*	Absorption in 80% IPA ppm SO_3†	Source
21	1.1	2.2	Oil
22	6.3	2.2	
23	5.9	2.5	
24	5.5	2.7	
27	5.9	6.9	
28	5.7	3.1	
51	7.5	4.0	
52	6.2	4.0	
53	5.6	3.8	
54	6.6	3.2	
55	7.3	3.3	
56	8.2	4.8	
11	3.7	3.4	Controlled Coal
12	6.1	3.7	
13	2.4	2.2	
14	1.5	6.1	
15	7.9	5.1	
16	4.5	6.5	
39	0.7	8.8	Uncontrolled Coal
40	1.6	9.6	
41	3.2	3.4	
43	1.6	5.0	
44	0.5	2.4	
45	2.6	3.2	
47	5.6	5.9	
48	5.0	4.8	
49	2.1	8.8	
50	3.8	8.1	

---

*Analytical Method - Barium Chloranilate

†Analytical Method - Ba^{++} Titration

1.8 SO_2 RESULTS OBTAINED IN THE WALDEN PILOT PLANT AND LABORATORY

1.8.1 Description of Pilot Plant

A photograph of the Walden combustion pilot plant is shown in Figure 1-15. The unit consists of a 400,000 Btu/hour (Jackson and Church) furnace with a combination gas/oil burner. The waste heat is discharged and the exhaust gas from the burner is passed into a series of carbon steel test sections three feet in length and eight inches in diameter. The flue gas is cooled down to about 300°F by an air-cooled heat exchanger and passed into a second series (3) of carbon steel test sections (sampling areas). The gas is pulled out of these test sections by a Westinghouse induced draft fan and exhausted through corrugated pipe at roof level.

Detailed schematics of the sampling test sections and pilot plant are shown in Figures 1-16 and 1-17, respectively. Each of the test sections has four static ports which can be used for particulate or gas sampling.

The original burner was designed to burn either natural gas or #2 fuel oil. When firing #2 oil, the excess air was only 50% in excess of theoretical. Units of this size normally run at 100 to 150% excess air. The unit has been modified to attain better combustion. A 90 CFM fan was placed on the air intake to the fire box. Using this auxiliary fan, we are able to burn #4 fuel oil with good combustion efficiency at the highest oil flow of 3.6 gal/hr. With these large nozzles, the heat output is increased beyond the design capacity of the original unit. The Btu output was increased to 650,000 Btu/hr with three 1.2 gal/hour nozzles. The volumetric flow in the duct was increased to 160 CFM with the auxiliary fan. The pilot plant specifications are given in Table 1-31. The concentrations of some gaseous and particulate pollutants are given in Table 1-32 for oil and gas firing.

1.8.2 Supplementary Laboratory and Pilot Plant Studies

Some laboratory studies were conducted involving linearity of

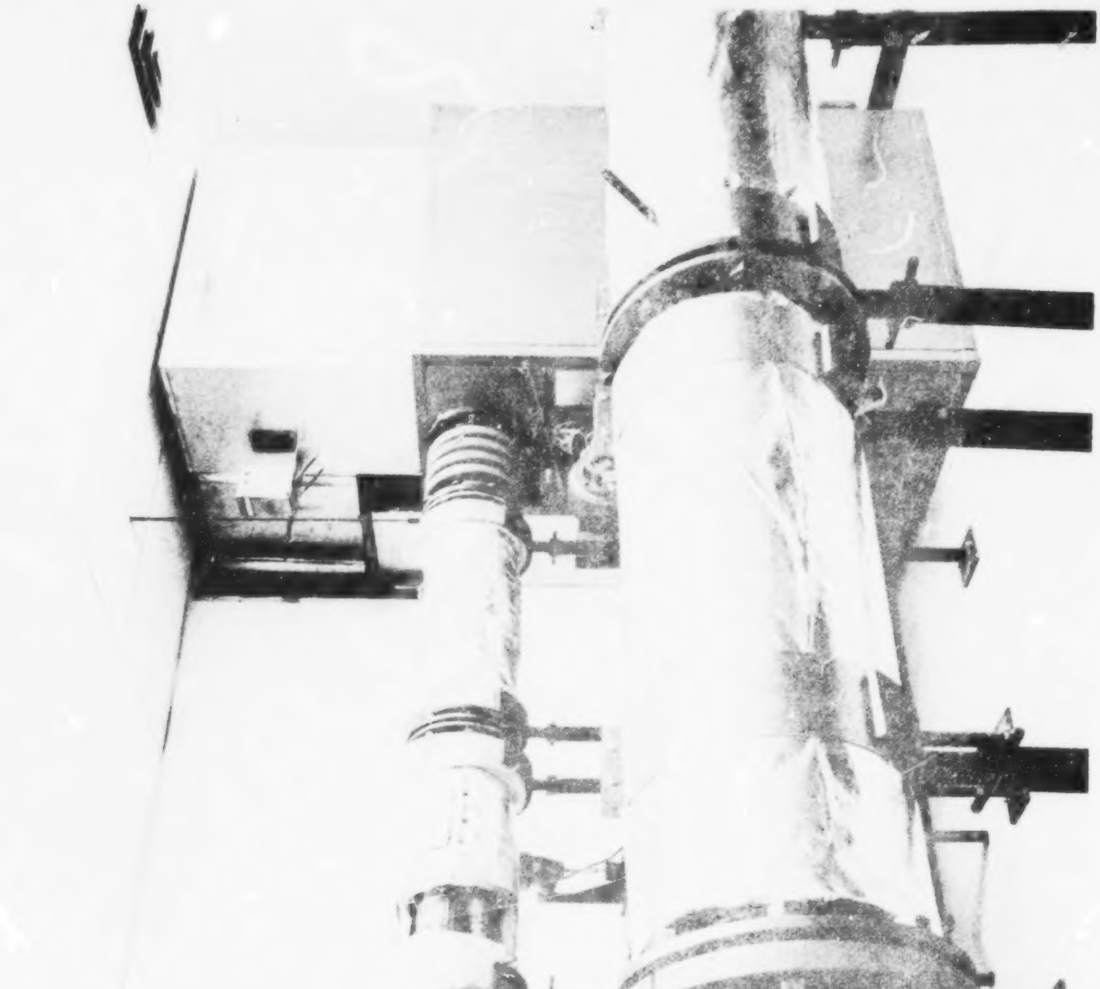


Figure 1-15. Walden Pilot Plant.

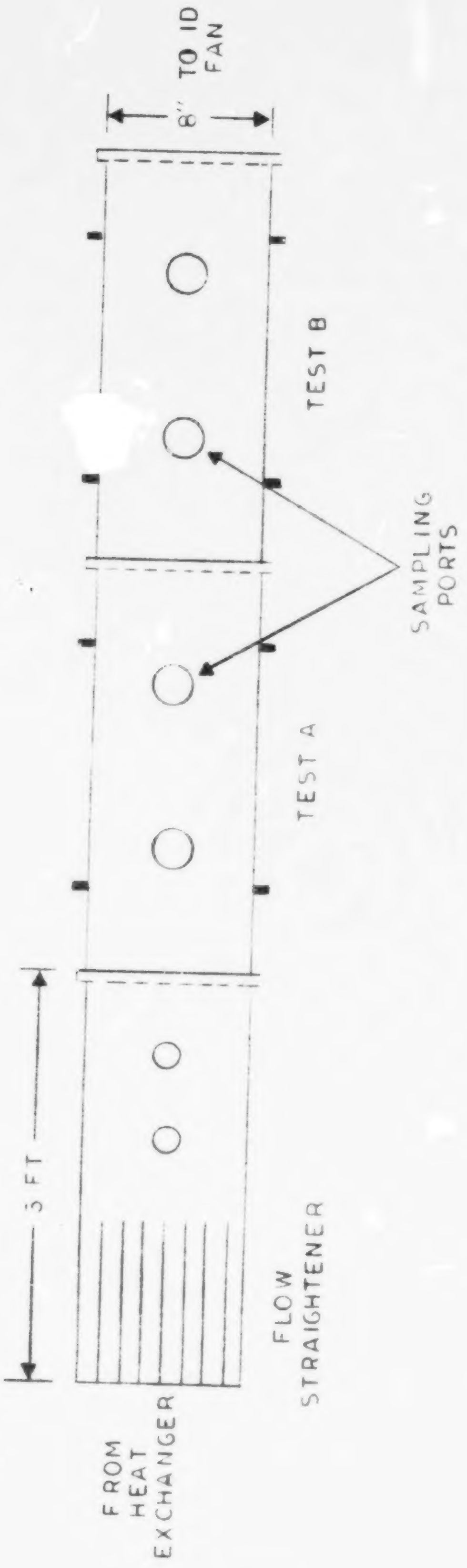

TO ID FAN
8"
TEST B
SAMPLING PORTS
TEST A
3 FT
FLOW STRAIGHTENER
FROM HEAT EXCHANGER

Figure 1-16. Pilot Plant Test Section Assembly.

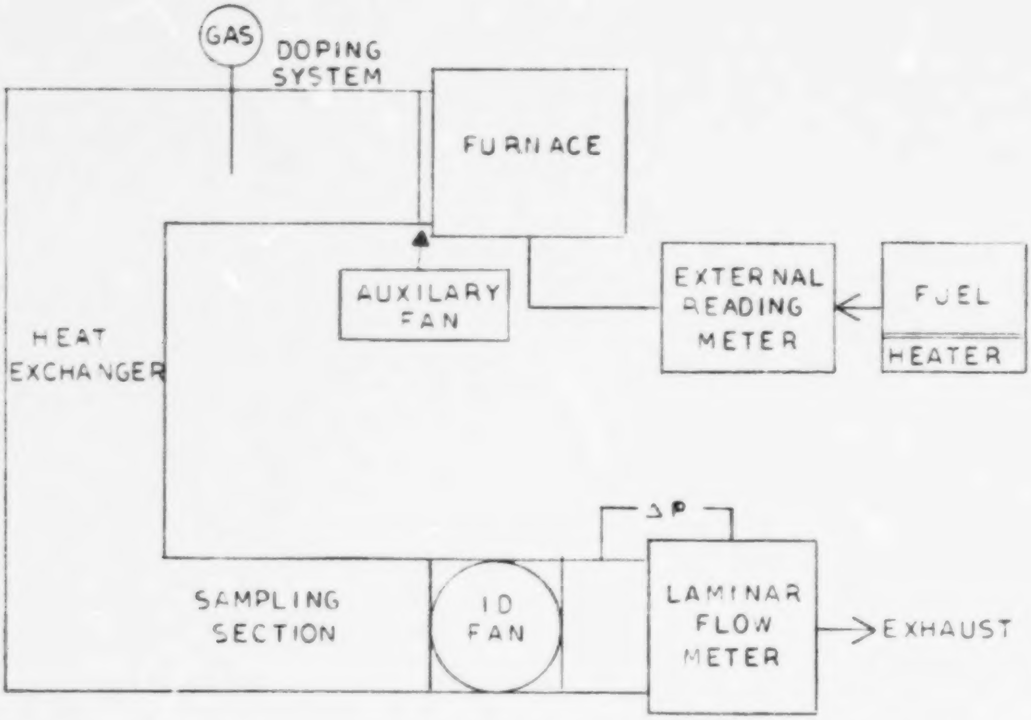

GAS
DOPING SYSTEM
FURNACE
AUXILARY FAN
EXTERNAL READING METER
FUEL
HEATER
HEAT EXCHANGER
ΔP
SAMPLING SECTION
ID FAN
LAMINAR FLOW METER
EXHAUST

Figure 1-17. Pilot Plant Schematic.

TABLE 1-31

PILOT PLANT SPECIFICATIONS

1. FURNACE
   200,000-650,000 Btu/hr input; gas, #2, #4, and possibly #6 fuel oil
   Warm air space heater
   Flue gas exit temperature 900°F
2. HEAT EXCHANGER
   Duty - cool flue gases from 900 to 275°F
   Heat duty 56,000 Btu/hr
3. TEST SECTIONS
   See separate drawings for details
   Hot test section: Temperature 600-900°F (depending on fuel flow rate and composition)
   Diameter = 8"
   Cold test section: Temperature 300°F
   Diameter = 8"
   Gas velocity from ∿ 3 to 10 ft/sec
4. F1, F2, F3
   Flow meters to measure fuel and combustion air flow rates
   F1 range: Direct reading meter for measuring flows of #2 and #4 oil from 0.25 to 5 GPH
   F2 range: 2000-10,000 SCFH (for flue gas)
   F3 range: 500-190 SCFH (of natural gas)
5. F4
   Flue gas flow rate - system will operate from 4900 to 7500 SCFH on oil and from 2500 to 5000 SCFH on gas.
6. T1
   Temperature control system; controls cooling air
   Flow rate to maintain 900°F temperature in exit from the furnace
7. T2
   Temperature control system; controls cooling medium flow rate to heat exchanger to maintain flue gas temperature exit from 325 to 150°F
8. T,P
   Temperature and pressure sensors
   Temperature: Max. 900°F; min. 150°F
   Pressure: Approximately atmospheric

TABLE 1-32

CHARACTERISTICS OF THE PILOT PLANT ON #2 OIL AND GAS

	Fuel Oil	Gas
Particulate	0.008 gr/SCF	
Hydrocarbon (ppm)*	∿ 2-5	∿ 0.5-5
NO_x	50	40
CO	200-1000	50-500
Maximum Temperature (°F) (hot section)	∿ 900	∿ 750
Maximum Flow (CFM)	150	120

---

*After steady-state conditions are attained.

the colorimetric method, collection efficiency and required flushing times for 80% IPA absorption.

Some early laboratory work on the barium chloranilate method for sulfate indicated that the calibration curve was linear up to 500 µg/ml of sulfate. Using calibration curves prepared for sulfate concentrations *up to 500 µg/ml*, least square slopes of about 480 µg/ml/abs unit were obtained. The data in Figure 1-18 yields a slope of ∿ 500 µg/ml/abs unit. Since this difference may amount to as much as 10 to 15% of the SO_x concentration, a detailed study of the linearity of the barium chloranilate method was conducted. We found that the method started to deviate from linearity between 350 and 400 µg/ml of sulfate. The deviation from Beer's law is not unusual. The positive deviation above ∿ 400 µg/ml indicates an ionic strength effect (Barney, 1964). This leads to the lower value of the slope (480 µg/ml) if concentrations above 350 µg/ml are used for preparation of the calibration curve. The slope is ∿ 500 µg/ml/abs unit if extrapolated *from* sulfate levels below 350 µg/ml. Thus, the correct slope is 500 µg/ml/abs unit at pH 5.6 and the method is linear *only* to 360 µg/ml. This value is in agreement with that of Barney (1964) and Kanno (1964).

Some data on the collection efficiency of H_2O_2 as a function of SO_2 concentration was determined. This will be discussed in detail in Section 1.8.3.

A series of tests were run in the pilot plant with gas firing and SO_2 doped up to 600 ppm. Note that *no SO_3* was added. The SO_2 was added into the duct at a low temperature (650°F), therefore, no oxidation is likely to occur. The sampling train consisted of two 80% IPA impingers in an ice bath followed by two peroxide impingers in series. The isopropanol impingers were removed from the ice bath and, after the appropriate flushing time, were treated with peroxide to oxidize any dissolved SO_2 to sulfate. The sulfate concentration was determined with the barium ionthorin titration. These data are given in Table 1-33 and plotted in Figure 1-19. We see that after flushing the IPA impingers for 15 minutes at 1 liter/min (this represents an equal volume of clean air since 15 liters

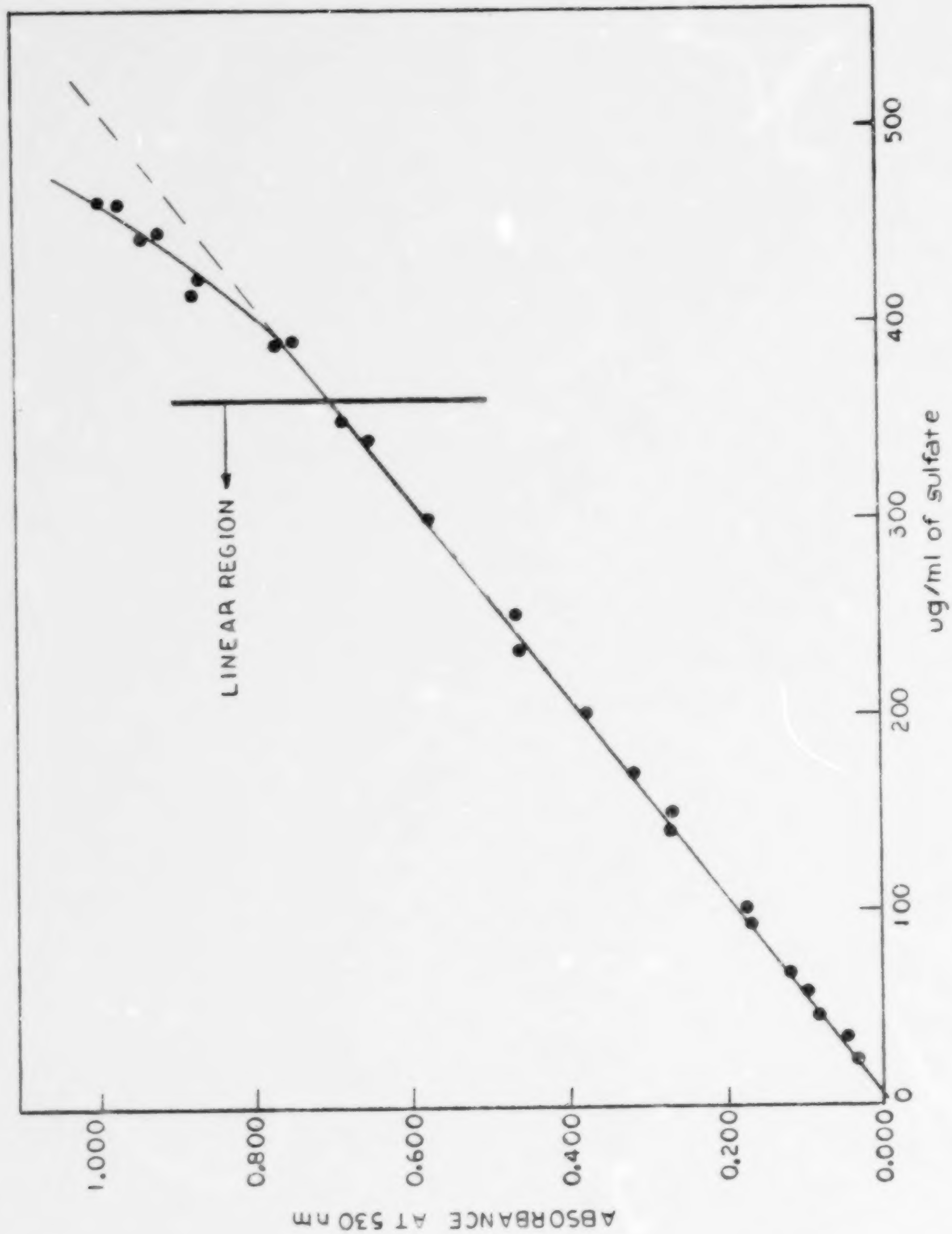


Figure 1-18. Linearity of the Calibration Curve for the Barium Chloranilate Method.

TABLE 1-33

EFFECT OF FLUSHING TIME ON THE SO_2 CONCENTRATION IN THE 80% ISOPROPANOL-20% WATER ABSORBER

Run No.	Flushing Time (min)*	ppm SO_2 in 80% IPA	ppm SO_2 in H_2O_2	% SO_2 in the 80% IPA
09-2	0	100	407	25
09-4	0	83	387	21
010-2	0	82	412	20
010-4	0	75	383	20
011-2	0	80	438	15
011-4	0	80	370	18
012-2	0	72	421	15
012-4	0	120	342	26
013-2	5	93	380	20
013-4	5	59	442	12
014-2	5	12	338	4
014-4	5	26	438	6
015-2	10	7	524	1
015-4	10	6	428	1
016-2	10	14	503	3
016-4	10	22	432	5
017-2	16	7	427	2
017-4	16	5	430	1
018-2	25	15	424	3
018-4	25	4	372	1

---

*At a rate of 1.0 l/min

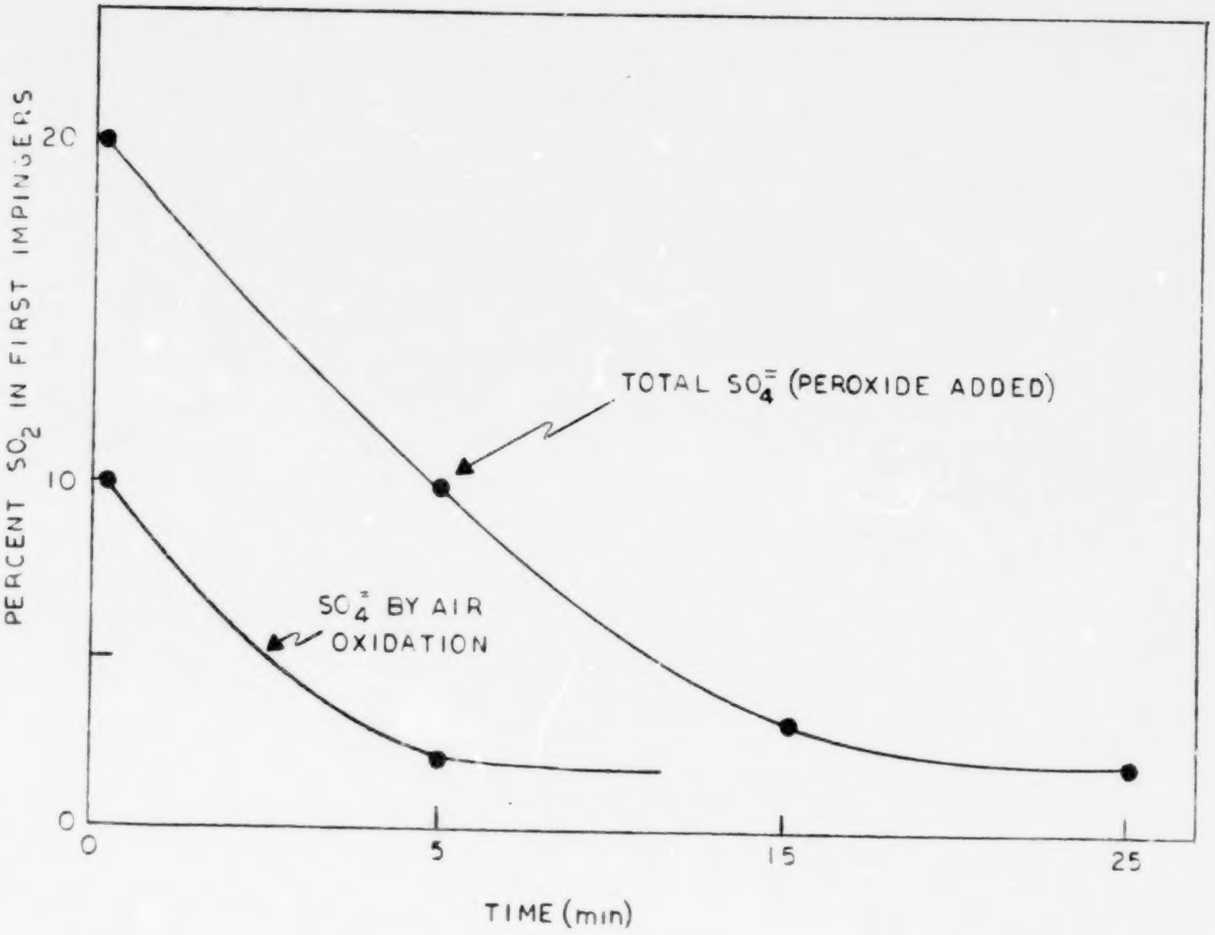


Figure 1-19. Effect of Flushing Time on the SO_2 in 80% IPA.

of flue gas were collected), the initial SO_2 concentration in the IPA dropped from 20 to 2% of the SO_2 concentration in the hydrogen peroxide.

The data in Table 1-33 represent the maximum sulfate concentrations to be expected since all the dissolved SO_2 was purposely oxidized to sulfate. However, two runs at ∿ 500 ppm SO_2 which were flushed for five minutes and analyzed the following day gave 7 and 9 ppm sulfate in the IPA. No peroxide was added to these samples. This is interesting in view of the fact the SO_3 in fossil fuel-fired plants is ∿ 2% of the SO_2. Here with *no SO_3* added, the residual sulfate (due to oxidation of dissolved SO_2) amounts to 1% of the SO_2. Since no metals nor SO_3 was present, the $SO_4^=$ came from the oxidation of SO_2 by air. *These results raise some doubt about the accuracy of the SO_3 determination if 80% IPA absorption is used.*

One additional problem which was observed was the difficulty with the barium ion titration at SO_2 concentrations below 50 ppm. The endpoint becomes very indistinct and difficult to reproduce with different operators at these low levels.

1.8.3 Effect of NO_x on SO_2 Methods and Accuracy Studies

The concentration of oxides of nitrogen may vary from several hundred to about 1500 ppm in large coal-fired power plants (Driscoll and Berger, 1971). Nitric oxide could interfere in the NaOH titration by being oxidized to NO_2 and reacting with water to form HNO_3.

The pilot plant was fired on gas and the flue gas was doped with SO_2 and NO. The total volumetric flow in the pilot plant was determined by stoichiometry with SO_2 and NO being added with calibrated rotameters. Initially, the accuracy of the methods were determined as a function of the SO_2 concentration with no addition of NO_x (just the background from the furnace). The data are given in Table 1-34. A total sample volume of 15 liters was collected at a flow rate of 1.0 liter/minute. Samples 60-1 and 60-2 represent results from two parallel trains (peroxide impingers) run off the same probe.

TABLE 1-34

EFFECT OF NO_x ON WET CHEMICAL METHODS FOR SO_2

Sample No.	ppm NO_x	Theoretical ppm SO_2	ppm SO_2 (NaOH)	ppm SO_2 (Ba^{++})	ppm SO_2 (Ba Chlor)
60-1	∼ 40	306		326	272
60-2	∼ 40	306		263	240
61-1	∼ 40	306		280	249
61-2	∼ 40	306		274	253
62-1	∼ 40	306		259	267
62-2	∼ 40	306		264	256
63-1	∼ 40	612		524	525
63-2	∼ 40	612		524	534
64-1	∼ 40	612		536	523
64-2	∼ 40	612		556	543
65-1	∼ 40	612		570	543
65-2	∼ 40	612		523	472
66-1	∼ 40	968		799	818
66-2	∼ 40	968		834	800
67-1	∼ 40	968		848	850
67-2	∼ 40	968		806	776
68-1	∼ 40	968		871	811
68-2	∼ 40	968		868	808
69-1	∼ 40	1246		1184	1090
69-2	∼ 40	1246		1193	1117
70-1	∼ 40	1246		1136	1101
70-2	∼ 40	1246		1248	1113
71-1	∼ 40	1246		1146	1071
71-2	∼ 40	1246		1147	1102
72-1	∼ 40	1590		1530	1438
72-2	∼ 40	1590		1520	1444
73 1	∼ 40	1590		1298	1211
73-2	∼ 40	1590		1521	1466
74-1	∼ 40	1590		1390	1346
74-2	∼ 40	1590		1431	1394
75-1	356	360	300	299	286
75-2	356	360	310	302	288
76-1	356	360	351	350	348
76-2	356	360	352	355	347
77-1	356	410	336	318	308
77-2	356	410	318	321	308
78-1	618	387	373	383	385
78-2	618	387	254	264	259
79-1	618	268	272	281	278
79-2	618	268	283	291	273
80-1	618	300	267	264	267
80-2	618	300	271	275	252

TABLE 1-34 (continued)

Sample No.	ppm NO_x	Theoretical ppm SO_2	ppm SO_2 (NaOH)	ppm SO_2 (Ba^{++})	ppm SO_2 (Ba Chlor)
81-1	990	333	388	301	271
81-2	990	333	336	342	328
82-1	990	347	318	330	314
82-2	990	347	342	344	340
83-1	990	344	339	341	324
83-2	990	344	346	349	340

The percent of theoretical SO_2 measured by Ba^{++} titration increases from 90% at 300 ppm to 95% above 1000 ppm. The barium chloranilate method yields slightly lower results with values ranging from 84% at 300 to 92% of theoretical SO_2 above 1000 ppm. Nitric oxide has no effect on any of the wet chemical methods as demonstrated from the data in Table 1-34 (runs 75-83). Note that the ratio of Ba^{++}/NaOH or Ba^{++}/Ba Chlor remains essentially constant over the entire range. "T" tests (to be described later in this section) indicate no significant difference between any of the methods as a function of NO_x level. The average percent theoretical (accuracy) for the methods at about 350 ppm is as follows:

Ba^{++} titration	92% accurate
NaOH titration	92% accurate
Ba Chlor	88% accurate

The "accuracy" appears to increase slightly as the SO_2 level is increased (runs 63-74), accuracies of 95 and 92% are observed for Ba^{++} and Ba Chlor, respectively.

In the above work, we have shown that the wet chemical methods for SO_2 yield about 90% of the theoretical SO_2 values at ∿ 300 ppm and ∿ 95% of the theoretical SO_2 above 1000 ppm SO_2. One reason for this low recovery of SO_2 could be a reduced collection efficiency at lower SO_2 concentrations. Therefore, we titrated the sulfate (SO_2) in the impingers separately instead of combining them for a series of tests. The collection efficiency was determined from pilot plant studies assuming that *all* the SO_2 was collected in the two impingers, and the fraction collected in impinger 1 divided by the total was the collection efficiency. The data in Table 1-35 show that the collection efficiency is 98% at both ∿ 500 and 1100 ppm SO_2. Thus, the decreased accuracy cannot be explained on the basis of reduced collection efficiency.

In another program (Driscoll, et al., 1972), we have investigated the accuracy of the Ba^{++} method by sulfur in fuel plus stoichiometry rather than direct addition of SO_2. Fuel oils (#2 and #4) were burned at

TABLE 1-35

DETERMINATION OF COLLECTION EFFICIENCY OF SO_2 IN AQUEOUS HYDROGEN PEROXIDE SOLUTION

ppm SO_2			
H_2O_2 Impinger 1	H_2O_2 Impinger 2	Total ppm SO_2	Collection Efficiency (%) $\left(\frac{SO_2\ \text{Impinger 1}}{\text{Total } SO_2}\right)$
394	44	448	88
364	6	370	98
415	6	421	96
336	6	342	98
380	0	380	100
434	8	442	98
338	0	338	100
433	5	438	99
524	0	524	100
425	3	428	99
499	4	503	99
432	0	432	100
427	0	427	100
430	0	430	100
424	0	424	100
372	0	372	100
1062	0	1062	100
1294	0	1294	100
852	0	852	100
1048	26	1074	98
1117	21	1138	98
1452	19	1471	99
1162	21	1183	98
1340	20	1360	99
1176	48	1224	96
1169	10	1179	99
1300	10	1310	99
1204	3	1207	100
1348	28	1378	98
1231	19	1250	98
1282	8	1290	99
1060	6	1066	100

Sample rate 1.0 l/min
Sampling time 15 min

various levels of excess air. The results are shown in Table 1-36. The percent theoretical obtained is 95% although lower SO_2 levels were present in the duct. Thus, some of the reduced accuracy at low (300 ppm) SO_2 levels with gas firing may be due to flow meter fluctuations, etc. It is not unreasonable, on the basis of the present data, to estimate the accuracy of the wet chemical methods as 95 ± 5%.

The following is a detailed statistical analysis of the pilot plant data which appeared in Table 1-34. The data were analyzed to determine the statistical significance of the differences between various SO_2 measurement procedures carried out under various conditions. The statistical analyses and their results are presented below.

Comparison of Ba^{++} and Ba Chlor as a Function of SO_2 Concentration

The data in Table 1 [illegible] represent 30 paired samples. Each pair represents analyses by each of the two methods on one effluent sample. The following procedures were used to compare methods.

(a) Hypothesis: $\mu_1 = \mu_2$

Reject hypothesis when

$$t \leq -t(1-\alpha/2)(29) \quad \text{or} \quad t \geq t(1-\alpha/2)(29)$$

where μ_1, μ_2 are means of the measurements for the two sampling methods; $t(1-\alpha/2)(29)$ is cumulative t-distribution for significance level α and 29 degrees of freedom; $t = \overline{D}/S_{\overline{D}}$; $\overline{D}$ is the mean of the differences between the paired samples (Di's); and $S_{\overline{D}}$ is the standard deviation of the Di's.

(b) Hypothesis: $\sigma_1 = \sigma_2$

Reject hypothesis when

$$F \leq F(\alpha/2)(29,29) \quad \text{or} \quad F \geq F(1-\alpha/2)(29,29)$$

where σ_1, σ_2 are the standard deviations of the measurements for the

TABLE 1-36

PILOT PLANT COMPARISON OF THEORETICAL SO_2 VERSUS PPM SO_2 MEASURED BY WET CHEMISTRY

Fuel		ppm SO_2 by Ba^{++}		Theoretical ppm SO_2	% Theoretical
#2 Oil 0.75 nozzles	1	149 141	145	122	119
	2	137 143	140	122	115
	3	119 123	121	122	99
#2 Oil (0.75 nozzles) change excessive air	4	96 100	98	100	98
	5	79 79	79	100	79
	6	80 85	82	100	82
#2 Oil large (1.2) nozzles	7	136 134	135	145	93
	8	131 130	130	145	90
	9	116 124	120	145	83
	10	137 133	135	145	93
	11	106 102	104	145	72
	12	133 130	131	145	90

TABLE 1-36 (continued)

Fuel		ppm SO_2 by Ba^{++}		Theoretical ppm SO_2	% Theoretical
#4 Oil large (1.2) nozzles	13	293 295	294	260	113
	14	235 235	235	260	90
	15	274 262	268	260	103
	16	261 272	266	260	102
	17	272 269	270	260	103

Average % Theoretical = 95

From Driscoll, J. N., Final Report to SWRI, June 1972.

sampling methods; $F(\alpha/2)(29,29)$, $F(1-\alpha/2)(29,29)$ are cumulative F-distributions for significance level α and 29 by 29 degrees of freedom; F = ratio of sample variances of the two methods.

(c) To analyze the comparison as a function of SO_2 concentration, the values of the Di's were regressed on the SO_2 concentration levels (Ba^{++}). A slope of zero would imply that the difference between the methods is not a function of SO_2 concentration so the hypothesis here is that the slope of the regression line (β_1) is zero. (This hypothesis was not formally tested.)

Results

(a) Hypothesis: $\mu_1 = \mu_2$

$$t = \overline{D}/S_{\overline{D}} = \frac{-28.7}{39.0} = -\ 0.73$$

and

$$t(1-0.05/2)(29) = 2.045$$

Therefore, cannot reject hypothesis at 5% significance level, i.e., no significant difference between methods at 0.05 level.

(b) Hypothesis: $\sigma_1 = \sigma_2$

$$F = \left(\frac{452}{431}\right)^2 = 1.10$$

and

$$F(1-0.05/2)(29,29) = 2.07$$

Therefore, cannot reject hypothesis at 5% significance level, i.e., no significant difference between precision of methods at 0.05 level.

(c) Regression coefficient for Di's vs SO_2 level is 0.045. Therefore, difference between methods is not a significant function of SO_2 levels. (We have not formally tested this hypothesis.)

Comparison of Ba^{++}, Ba Chlor and NaOH Methods as a Function of NO_x Level

The data in Table 1-34 represent 18 samples. Each set of data represents analyses by each of the three methods on one effluent sample. Each of the three combinations of paired methods were analyzed by the following procedures.

(a) Hypothesis: $\mu_1 = \mu_2$

Reject hypothesis when

$t \leq -t(1-\alpha/2)(17)$ or $t \geq t(1-\alpha/2)(17)$

(b) Hypothesis: $\sigma_1 = \sigma_2$

Reject hypothesis when

$F \leq F(\alpha/2)(17,17)$ or $F \geq F(1-\alpha/2)(17,17)$

(c) Hypothesis: $\beta_1 = 0$ (regression of Di's on NO_x level)

(We have not formally tested this hypothesis.)

Results

(a) Hypothesis: $\mu_1 = \mu_2$

(i) NaOH method vs Ba^{++} method

$$t = \overline{D}/S_{\overline{D}} = \frac{-3.0}{7.6} = -0.39$$

and

$$t(\alpha = 0.05)(17) = 2.11$$

Therefore, cannot reject hypothesis, i.e., no significant difference.

(ii) NaOH method vs Ba Chlor method

$$t = \overline{D}/S_{\overline{D}} = \frac{18.4}{9.8} = 1.87$$

and

$$t(\alpha = 0.05)(17) = 2.11$$

Therefore, cannot reject hypothesis, i.e., no significant difference.

(iii) Ba^{++} method vs Ba Chlor

$$t = \overline{D}/S_{\overline{D}} = \frac{21.4}{8} = 2.67$$

and

$$t(\alpha = 0.05)(17) = 2.11$$

Therefore, reject hypothesis, i.e., there is a significant difference (Ba^{++} method higher than Ba Chlor) at the 0.05 level. However, $t(\alpha = 0.01)(17) = 2.890$ and, therefore, cannot reject it at the 0.01 level.

(b) Hypothesis: $\sigma_1 = \sigma_2$

(i) NaOH method vs Ba^{++} method

$$F = \left(\frac{35.1}{34.5}\right)^2 = 1.06$$

$$F(\alpha = 0.05)(17,17) = 2.66$$

Therefore, cannot reject hypothesis, i.e., no significant difference.

(ii) NaOH method vs Ba Chlor method

$$F = \left(\frac{35.8}{35.1}\right)^2 = 1.04$$

$$F(\alpha = 0.05) = 2.66$$

Therefore, cannot reject hypothesis, i.e., no significant difference.

(iii) Ba^{++} method vs Ba Chlor method

$$F = \left(\frac{35.8}{34.5}\right)^2 = 1.08$$

$$F(\alpha = 0.05)(17,17) = 2.66$$

Therefore, cannot reject hypothesis.

(c) Hypothesis: $\beta_1 = 0$

(i) NaOH method vs Ba^{++} method

$$B_1 = 0.015$$

Therefore, difference between methods is not significant function of NO_x level.

(ii) NaOH method vs Ba Chlor method

$$B_1 = 0.005$$

Therefore, difference is not significant function of NO_x level.

(iii) Ba^{++} method vs Ba Chlor method

$$B_1 = 0.01$$

Therefore, difference is not significant function of NO_x level.

Additional statistical data are given in Tables 1-37 and 1-38 on the effect of NO_x doping. The precision is essentially the same as a function of NO_x level and the regression analyses and correlation coefficients (Table 1-38) indicate that all three methods are in good agreement with each other.

1.8.4 Effect of HCl on the Accuracy of SO_2 Methods

1.8.4.1 Introduction

Chlorides (such as NaCl and KCl) as well as chlorine are present in coal and are converted to HCl during combustion (Iapalucci, Demski and Bienstock, 1969). The effect of HCl was studied since it was expected to be an interference with the NaOH titration procedure. The

TABLE 1-37

PILOT PLANT RESULTS - PRECISION WITH NO_x DOPING

Analytic Method	Runs	# Samples	ppm NO_x	mean ppm SO_2	Standard Deviation	CV
Barium Chloranilate	60-62	6	∿ 40	235	7.3	3.1
	63-65	6	∿ 40	523	7.7	1.5
	66-68	6	∿ 40	811	10.6	1.3
	69-71	6	∿ 40	1099	9.5	0.9
	72-74	6	∿ 40	1384	8.7	0.6
Ba^{++} Titration	60-62	6	∿ 40	278	15.2	5.5
	63-65	6	∿ 40	544	15.5	2.9
	66-68	5	∿ 40	838	38.7	4.6
	69-71	5	∿ 40	1161	25.7	2.2
	72-74	6	∿ 40	1448	27.2	1.9
NaOH Titration	60-62	6	∿ 40	189	12.0	6.3
	63-65	4	∿ 40	357	6.1	1.7
	66-68	5	∿ 40	480	10.6	2.2
	69-71	6	∿ 40	677	9.8	1.4
	72-74	6	∿ 40	900	12.8	1.4
NaOH Titration	75-77	6	356	328	2.6	0.8
	78-80	6	618	287	9.5	3.3
	81-83	6	990	328	8.9	2.7
Ba^{++} Titration	75-77	6	356	324	2.8	0.9
	78-80	6	618	293	3.4	1.2
	81-83	6	990	335	4.0	1.2
Barium Chloranilate	75-77	6	356	278	4.4	1.6
	78-80	6	618	236	3.6	1.5
	81-83	6	990	283	5.9	2.1

TABLE 1-38

REGRESSION EQUATIONS AND CORRELATION COEFFICIENTS FOR A GAS-FIRED PILOT PLANT

Methods Compared	Sample No.	Dopant	Correlation Coefficient	Regression Equation
Ba^{++} Titration (x) and Ba Chloranilate (y)	60-74	(just SO_2)	0.997	y = 0.96 x -11.7
Ba^{++} Titration (x) and Ba Chloranilate (y)	75-83	NO_x	0.974	y = 0.929 x -23.3
Ba^{++} Titration (x) and NaOH Titration (y)	75-83	NO_x	0.819	y = 0.915 x +29.4
Ba Chloranilate (x) and NaOH Titration (y)	75-85	NO_x	0.961	y = 1.04 x +31.7
Ba^{++} Titration (x) and Ba Chloranilate (y)	85-100	HCl	0.890	y = 1.07 x -33
Ba^{++} Titration (x) and NaOH Titration (y)	85-100	HCl	0.680	y = 0.810 x +96
Ba Chloranilate (x) and NaOH Titration (y)	85-100	HCl	0.810	y = 0.87 x +81
Ba^{++} Titration (x) and Ba Chloranilate (y)	101-113	HOAc	0.970	y = 0.879 x -8.75
Ba^{++} Titration (x) and NaOH Titration (y)	101-113	HOAc	0.803	y = 0.778 x +43.9
Ba Chloranilate (x) and NaOH Titration (y)	101-113	HOAc	0.766	y = 0.850 x +41.7

chlorine content of some American coals is given in Table 1-39 and is seen to vary from 0.01 to 0.5%. British coals are generally higher in chlorine content than American coals (Smith and Gruber, 1966). The British coals are classified with regard to chlorine content as follows: high, over 0.3%; medium, 0.15-0.3%; low, below 0.15%.

Ten coals containing various levels of chlorine were burned in a pilot plant at the BuMines to determine the behavior of chlorine in coal combustion (Iapalucci, Demski and Bienstock, 1969). A detailed analysis of the composition of the various coals is given in Table 1-40. Earlier work had shown that one of the products of combustion of chlorine containing coals was HCl. Iapalucci, Demski and Bienstock (1969) used both mass spectrophotometric and wet chemical (Volhard titration) techniques for analysis of flue gas samples. HCl was the only product detected from the combustion of chlorine containing coals. They calculated the equilibrium distribution for a number of chlorine containing compounds using a computer program.

These data are given in Figure 1-20. Although Cl_2, HOCl, and NaOCl are possible products, none of these compounds were detected. However, analytical methods employed may not have been sensitive enough to detect them. Sampling at a large power plant showed that only 1.5% of the chlorine was retained in the ash with the remainder (∿ 90%) being emitted as HCl (Iapalucci, et al., 1969).

In Table 1-40, we note that the maximum Cl/S ratio in the coal is 0.39. When this is converted to Cl/SO_2, the value becomes ∿ 0.195.

These coals were selected by BuMines as typical, and the chlorine contents probably represent the maximum amount of hydrogen chloride evolution. If we analyze the data in Table 1-40 and determine the HCl/SO_2 ratio, we find that for the five high sulfur coals ($S > 2\%$) the calculated HCl value is $2.5 \pm 0.9\%$ of the SO_2 concentration. Thus, the interference for an acid-base titrametric procedure would be minimal (less than 3%). For the low sulfur coals ($S = 1\%$ or less), however, the Cl/S ratio

TABLE 1-39

CHLORINE CONTENT OF VARIOUS COALS*

Source of Coal		
State	Bed	Chlorine Content, %
Ohio	Sharon	0.01
Illinois	No. 6	0.01
Indiana	No. 4	0.06
West Virginia	Pittsburgh	0.07
Pennsylvania	Lower Freeport	0.14
Illinois	Central Illinois	0.35
Oklahoma	Henryetta	0.46

---

*Taken from "Atmospheric Emissions from Coal Combustion," by W. S. Smith and C. W. Gruber, Pub. #999-AP-24 by PHS (April 1966).

TABLE 1-40

COMBUSTION OF PULVERIZED COALS

Coal seam, county, and State	Beckley, Wyoming, W. Va.	Upper Freeport, Cambria, Pa.	Sewell, Fayette, W. Va.	Upper Kittanning, Cambria, Pa.	Illinois #6, Jefferson, Ill.	Pittsburgh, Allegheny, Pa.	Lower Kittanning, Indiana, Pa.	Upper Freeport, Preston, W. Va.	Upper Freeport, Clarion, Pa.	Middle Kittanning, Clarion, Pa.
ASTM designation, D388-66....	Lvb	Lvb	Mvb	Mvb	Hvab	Hvab	Hvab	Hvab	Hvab	Hvbb
Mine..........................	West Gulf	Sonman	Lochgelly	Piper	Orient #3	Champion #1	Arcadia	Borgman	Bish #3	Sunny Hill
Coal analysis, as received, wt pct:										
Hydrogen..................	4.5	4.3	5.0	4.8	5.5	5.2	4.8	4.9	5.1	4.4
Carbon....................	82.0	77.9	85.5	82.2	72.1	75.3	74.2	75.1	72.3	55.6
Nitrogen..................	1.6	1.1	1.6	1.5	1.7	1.5	1.5	1.4	1.4	1.0
Oxygen....................	6.3	3.7	4.3	[illegible]	14.3	8.3	6.2	3.7	7.2	9.9
Sulfur....................	0.9	1.3	0.62	0.7	1.1	1.9	2.3	3.4	2.1	6.5
Chlorine..................	0.11	0.12	0.27	0.13	0.39	0.08	0.16	0.17	0.13	0.14
Ash.......................	4.7	11.7	3.0	7.1	5.3	7.8	11.2	11.5	11.9	22.6
Sodium..................	0.10	0.05	0.08	0.08	0.17	0.12	0.15	0.16	0.15	0.24
Potassium...............	0.11	0.07	0.05	0.07	0.10	0.06	0.21	0.16	0.27	0.45
Magnesium...............	0.02	0.02	0.04	0.01	0.02	<0.01	0.02	0.02	0.02	0.04
Calcium.................	0.09	0.15	0.11	0.12	0.04	0.09	0.08	0.05	0.05	0.1
Proximate analysis, wt pct:										
Moisture..................	3.6	1.1	0.7	0.6	6.7	1.6	2.0	0.7	1.6	3.2
Volatile matter...........	18.5	18.5	25.8	20.4	36.9	36.1	28.4	27.4	34.5	35.8
Fixed carbon..............	73.2	68.7	70.5	71.9	51.1	54.5	58.4	60.4	52.0	38.4
Ash.......................	4.7	11.7	3.0	7.1	5.3	7.8	11.2	11.5	11.9	22.6
Proximate analysis, Btu......	14,470	13,440	15,030	14,400	12,850	13,520	13,210	13,440	12,930	10,150
Recovery in ash, percent:										
Chlorine..................	7.1	3.9	4.4	2.2	5.6	4.9	1.9	4.8	1.6	3.5
Sulfur....................	8.1	7.1	7.9	10.7	6.3	5.3	4.6	6.3	2.3	4.6
Atom ratio, Cl/S:										
In coal...................	0.12	0.08	0.39	0.17	0.32	0.38	0.06	0.045	0.06	0.019
In ash....................	0.10	0.05	0.22	0.03	0.28	0.36	0.03	0.035	0.04	0.015
Carbon combustion efficiency, percent......................	95	95	95	95	94	95	97	94	99	98

From BuMines RI 7260 "Chlorine in Coal Combustion"

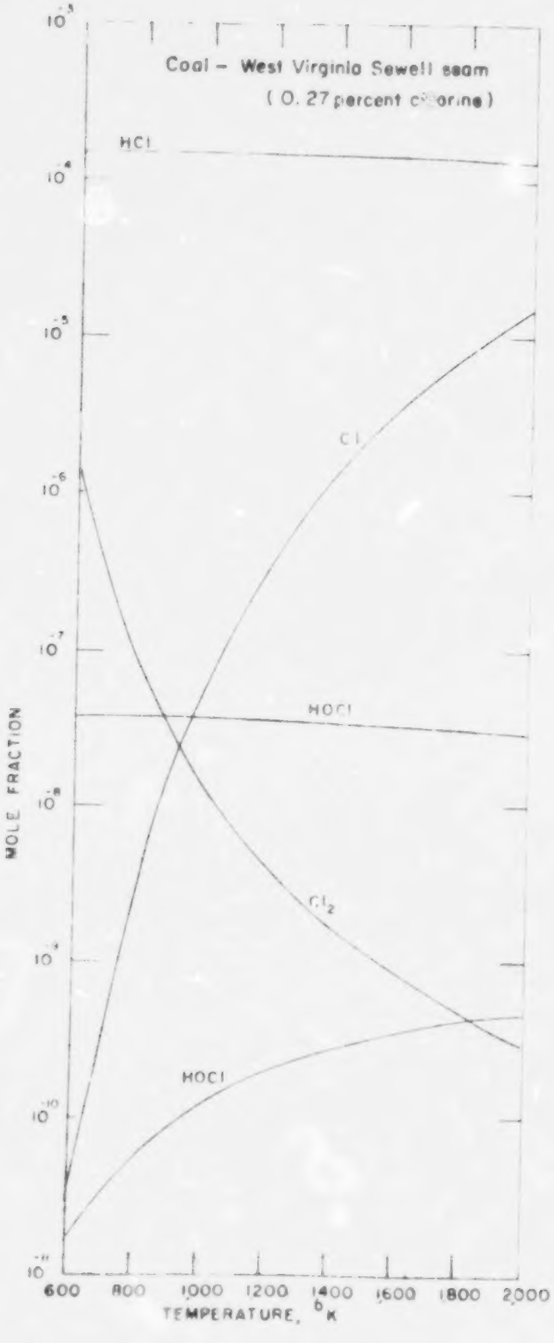


Figure 1-20. Equilibrium Distribution of Chlorine Compounds in the Combustion Gas of a Sewall Coal at 20 Percent Excess Air.

is considerably higher. The average values calculated from the data in Table 1-40 is $HCl/SO_2 = 12 \pm 8\%$. This would represent a significant error in the SO_2 measurement if an acid base titration were used for the analyses. In order to examine this effect, we investigated the effect of HCl on the wet chemical methods for SO_2 in the pilot plant. This is described in the following section.

1.8.4.2 Pilot Plant Results

The pilot plant results were obtained with the unit firing *gas* and doping the effluent with both SO_2 and HCl. Runs were made with two sets of impinger trains (filled with aqueous peroxide) in parallel. For these runs, a total sample volume of ~ 15 liters was collected at a flow rate of 1.0 liter/min. The data were taken at HCl concentrations varying from ~ 0 to 150 ppm with the SO_2 concentration at approximately 150 ppm.

We computed the HCl flow rates for the rotameter from the air calibration and calculated the expected HCl concentrations in the duct from the stoichiometric gas flow, excess air and temperature. The HCl concentration in the pilot plant flue gas was determined by bubbling a stream of the effluent through impingers containing distilled water. The chloride samples were analyzed using an Orion Model 94-17 chloride electrode. The potential was measured with an Orion Model 701 digital millivolt meter. The data which were obtained are given in Table 1-41. The agreement between the measured and calculated HCl values is excellent.

The SO_2 levels were kept between 300 and 400 ppm which are typical of effluents from fuel containing 0.5-1% sulfur.

The data obtained with SO_2 doping are given in Table 1-42. The barium chloranilate method yields results which are slightly lower than Ba^{++} with no HCl added. At 150 ppm HCl, no difference is observed or expected between these two sulfate specific methods.

The NaOH titration which is specific for H^+ rather than sulfate does show a marked difference compared to Ba^{++} between 0 and

TABLE 1-41

COMPARISON OF MEASURED AND CALCULATED HCl CONCENTRATIONS IN THE PILOT PLANT

ppm HCl	
Calculated from Stoichiometry	Measured with an Ion Selective Electrode
150	150
	140
	140
90	90
	90
40	47
	47

TABLE 1-42

EFFECT OF HCl ON WET CHEMICAL METHODS FOR SO_2

Sample No.	ppm HCl	ppm SO_2 (NaOH)	ppm SO_2 (Ba^{++})	ppm SO_2 (Ba Chlor)	Δ (NaOH-Ba^{++})
100a	0	340	337	318	3
100b	0	333	330	308	3
99a	0	343	339	331	4
99b	0	404	392	366	12
98a	40	318	286	307	32
98b	40	366	366	356	0
97a	40	-	-	354	-
97b	40	364	-	350	-
96a	40	160	136	104	24
96b	40	180	168	162	12
95a	40	160	139	-	21
95b	40	179	162	-	17
94a	90	305	264	237	41
94b	90	348	292	271	56
93a	90	312	286	283	26
93b	90	392	350	321	42
92a	150	-	312	325	-
92b	150	384	316	321	68
91a	150	334	288	235	56
91b	150	349	312	264	37
90a	150	426	373	365	53
90b	150	395	331	328	64
87a	150	454	400	404	54
87b	150	454	398	428	56
86a	150	464	414	415	50
86b	150	444	390	396	54
85a	150	442	365	363	77

HCl = X

Y = Δ

$\Delta = 5.42 + 0.35X$ (HCl)

Correlation Coefficient = 0.90

150 ppm HCl (Table 1-42). In this table, we have calculated the difference between NaOH and Ba^{++} titrations (Δ) and compared this to the HCl concentration. There is about 4 ppm difference at 0 ppm HCl and about 60 ppm difference at 150 ppm HCl. The regression equation for ppm HCl versus Δ(ppm SO_2 NaOH-ppm SO_2 Ba^{++}) is:

$$\Delta(\text{ppm } SO_2 \text{ NaOH-ppm } SO_2 \text{ } Ba^{++}) = 5.42 + 0.35\ (HCl)$$

The correlation coefficient for these values is 0.90.

Although a 1:1 correlation between Δ and HCl concentration might be expected, the chemistry of the system suggests a 0.5:1 ratio as follows:

$$H_2O_2 + 2H^+ + 2e^- \rightleftharpoons 2H_2O$$

$$2Cl^- - 2e^- \rightleftharpoons Cl_2$$

$$Cl_2 + H_2O \rightleftharpoons HOCl + HCl$$

Overall reaction

$$H_2O_2 + 2HCl + H_2O \rightleftharpoons HCl + HOCl + 2H_2O$$

The above reaction is spontaneous and indicates that the H_2O_2 reacts with Cl^-[*] to produce HOCl. Since this latter species is a weak acid, e.g., pK = 7.5, it will not react with NaOH (if bromphenol blue indicator is used). Thus, the value of the slope of 0.35 is quite reasonable as suggested by the above reaction. The data indicate that HCl is a potential interference with an acid base titration and that with low sulfur coals containing chlorine, errors from 5 to 15% could be expected.

If we examine the regression equations in Table 1-38 for HCl doping, we note that Ba^{++} or Ba Chlor vs NaOH have a considerable *bias* in the equations (intercepts of 96 and 81, respectively, and slopes which deviate considerably from unity). The sulfate method, however, show reasonably good agreement with each other for HCl doping.

---

[*] In another application, we have used Cl^- ion to decompose aqueous H_2O_2.

The precision of the barium titration with HCl does not change and is about ± 2%. The CV for the NaOH titration and Ba Chlor methods are slightly higher, e.g., 3.3 and 5.0%, respectively, than the values found in the field indicating a possibility of an interference or most probably, a small sample size (Table 1-43).

1.8.5 Effect of Organic Acids of SO_2 Methods

Organic acids have been reported as minor constituents in the effluents of coal-fired power plants. In units with poor combustion of fuel, high levels of hydrocarbons (partially organic acids) may be present.

The doping system for the organic acids (acetic acid) was set up in the pilot plant as shown in Figure 1-21. The acetic acid was heated to a constant temperature (about 43°C). The concentration of acetic acid could then be calculated from the vapor pressure of acetic acid at 43°C, the flow rate of air through the impinger, and the total volumetric flow in the duct (from stoichiometry). The acetic acid concentration was varied by increasing the flow rate of air through the impinger and keeping the acetic acid temperature constant. The acetic acid concentration in the duct was varied from several hundred to 1000 ppm (acetic acid). The results are given in Table 1-44. *Considerable difficulty was observed with the NaOH bromphenol blue endpoint even with low concentrations of acetic acid. The indicator color change was very gradual instead of sharp. This may be due to the buffering action produced by the weak acid.* The data in Table 1-44 show that the barium ion titration and barium chloranilate methods agree well with each other and do not seem to be affected by the very high concentrations of acetic acid. The statistical data in Table 1-38 bear this out. The correlation coefficient is high, 0.97, intercept is small and the slope is close to unity.

In the initial data (0 ppm HOAc) in Table 1-44, the NaOH titration gives lower SO_2 values than expected while Ba^{++} yields higher values. The reason for this is not known. As the acetic acid is increased, the NaOH gives slightly higher SO_2 values than either $SO_4^=$ method. The difference at about 1000 ppm AcOH is about 50 ppm or 20%. Levels this high are

TABLE 1-43

PILOT PLANT DOPING - PRECISION OF HCl AND HOAc DOPING

Analytic Method	# Samples	mean ppm SO_2	CV	Dopant
NaOH Titration	24	375	3.3%	HCl
Ba^{++} Titration	23	348	2.0%	HCl
Barium Chloranilate	24	344	5.0%	HCl
NaOH Titration	23	226	3.3%	HOAc
Ba^{++} Titration	23	240	4.0%	HOAc
Barium Chloranilate	24	210	4.3%	HOAc

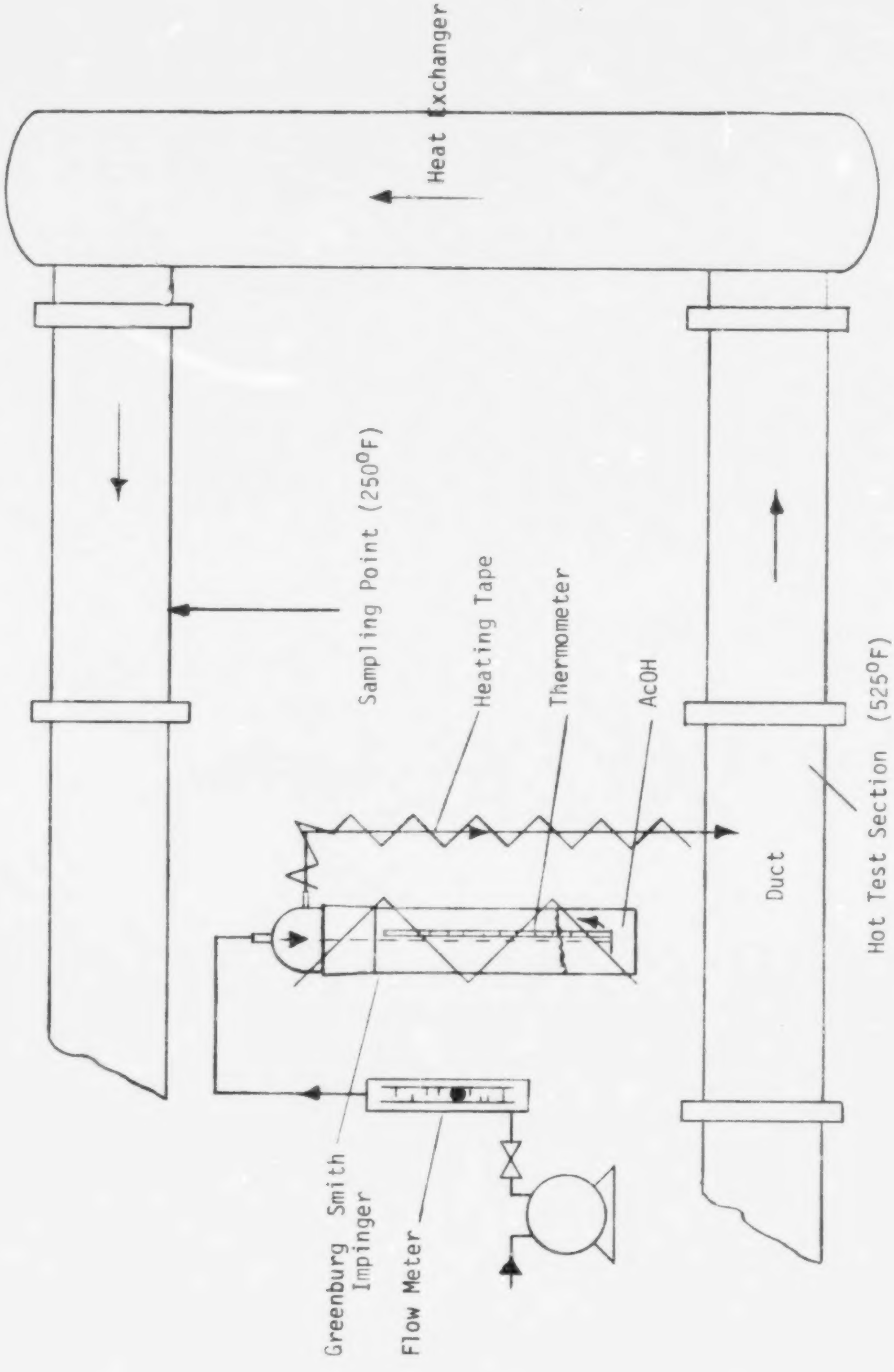

Heat Exchanger
Sampling Point (250°F)
Heating Tape
Thermometer
AcOH
Duct
Hot Test Section (525°F)
Greenburg Smith Impinger
Flow Meter

Figure 1-21. Doping System for Organic Acids.

TABLE 1-44

EFFECT OF ORGANIC ACIDS ON WET CHEMICAL METHODS FOR SO_2

Sample No.	ppm HOAc	Theoretical ppm SO_2	ppm SO_2 (NaOH)	ppm SO_2 (Ba^{++})	ppm SO_2 (Ba Chlor)
101-1	0	280	247	306	283
101-2	0	280		336	258
102-1	0	320	109	148	136
102-2	0	320	150	172	148
107-1	0	313	210	268	222
107-2	0	313	136	180	138
108-1	0	277	223	285	237
108-2	0	277	157	203	160
109-1	173	260	262	322	261
109-2	173	260	174	181	146
110-1	179	268	270	310	265
110-2	179	268	206	223	227
104-1	190	285	130	115	73
104-2	190	285	245	223	183
105-1	230	346	205	182	257
105-2	230	346	262	214	274
106-1	495	376	134	124	189
106-2	495	376	218	152	261
111-1	871	316	284	313	271
111-2	871	316	204	231	194
112-1	940	341	261	316	278
112-2	940	341	300	244	194
114-1	1045	278	260	199	199
114-2	1045	278	380	352	293
113-1	1360	363	319	306	287
113-2	1360	363	247	214	181

not likely to be encountered in a coal-fired power plant. The difference between the NaOH and the sulfate methods as evidenced in Table 1-44 is undoubtedly due to the obscuration of the endpoint mentioned earlier.

In the following paragraphs is a statistical evaluation of the data in Table 1-44 via the student "T" distribution.

Comparison of Ba^{++}, Ba Chlor and NaOH Methods as a Function of AcOH Level

The data in Table 1-43 represents 26 samples. Each set of data represents analyses by each of the three methods on one effluent sample. Each of the three combinations of paired methods were analyzed by the procedures outlined above. The NaOH data for sample 101-2 were omitted and, hence, a sample of 25 data points was available for those combinations involving NaOH method. In each case, the Di's were regressed on HOAc levels.

(a) Hypothesis: $\mu_1 = \mu_2$

(i) NaOH method vs Ba^{++} method

$$t = \overline{D}/S_{\overline{D}} = \frac{-7.6}{42.0} = -\ 0.18$$

and

$$t(\alpha = 0.05)(24) = 2.064$$

Therefore, cannot reject hypothesis, i.e., no significant difference.

(ii) NaOH method vs Ba Chlor method

$$t = \overline{D}/S_{\overline{D}} = \frac{-9.1}{45.6} = 0.20$$

and

$$t(\alpha = 0.05)(24) = 2.064$$

Therefore, cannot reject hypothesis, i.e., no significant difference.

(iii) Ba^{++} method vs Ba Chlor method

$$t = \overline{D}/S_{\overline{D}} = \frac{0.7}{47.5} = 0.015$$

and

$$t(\alpha = 0.05)(25) = 2.060$$

Therefore, cannot reject hypothesis, i.e., no significant difference.

(b) Hypothesis: $\sigma_1 = \sigma_2$

(i) NaOH method vs Ba^{++} method

$$F = \left(\frac{67.8}{65.7}\right)^2 = 1.06$$

and

$$F(\alpha = 0.05)(24,24) = 2.27$$

Therefore, cannot reject hypothesis.

(ii) NaOH method vs Ba Chlor method

$$F\ (\alpha = 0.05)(24,24) = 2.27$$

Therefore, cannot reject hypothesis.

(iii) Ba^{++} method vs Ba Chlor method

$$F = \left(\frac{69.5}{63.9}\right)^2 = 1.18$$

and

$$F(\alpha = 0.05)(25,25) = 2.27$$

Therefore, cannot reject hypothesis.

(c) Hypothesis: $B_1 = 0$

(i) NaOH method vs Ba^{++} method

$$B_1 = 0.04$$

Therefore, difference is not significant function of HOAc level.

(ii) NaOH method vs Ba Chlor method

$$B_1 = 0.05$$

Therefore, difference is not significant function of HOAc level.

(iii) Ba^{++} method vs Ba Chlor method

$$B_1 = 0.002$$

Therefore, difference is not significant function of HOAc level.

1.9 SUMMARY AND CONCLUSIONS

The ion exchange step which was included in the procedures for removing cationic interferences from the sulfate specific methods leads to a considerable loss of SO_2. The problem appears to be a swelling of the resin and subsequent irreversible adsorption of sulfate ions when peroxide is present. The *field* data for the sulfate specific methods on trains a and b had to be corrected for the loss of sulfate. In the pilot plant and other stationary source measurements (Section 2), the ion exchange step was eliminated and no corrections were necessary.

One of the three trains (train c) run in parallel which collected SO_3 by absorption in 80% isopropanol-20% water (IPA) was not flushed to remove the dissolved SO_2. The barium ion titration results from this train were considerably lower indicating the need for removing residual SO_2 from the SO_3 absorber.

Many of the field tests were conducted using critical orifices (Figure 1-5) as metering devices. The long-term calibration of a number of orifices used in the field was checked frequently and was found *not* to vary more than a few percent (Table 1-7) although as many as 25 to 50 SO_2 samples were run between calibrations. These devices appear to be very well suited for field use.

A major problem with the sampling was encountered at the inlet to a wet scrubber on a controlled coal-fired power plant. With the high sampling rate employed (3 to 4 liters/min), the dust ($CaCO_3$) collected on particulate filter and adsorbed SO_2.

At the outlet of the wet scrubber, no major problems were encountered with the sampling or analytical methods. The coefficient of variation (precision of replicate analysis) was 1 to 2% for barium ion and NaOH titration but 4 to 5% for the barium chloranilate method. This was traced to an interference from the particulate matter (Ca^{++}). This species does not interfere with either titration method but would interfere with the colorimetric procedure. Good agreement was obtained with all methods on analysis of aliquots of the same SO_2 sample. Some variation between methods was noted between trains, however.

At the oil-fired power plant, the coefficient of variation was 2 to 3% for both NaOH titration and barium chloranilate but only 1 to 2% for barium ion titration. All the methods are in excellent agreement with each other indicating, as expected, no potential interferences with any of the methods. The percent of theoretical SO_2 measured by Ba^{++} (train b) and Ba Chlor is greater than 100%. The NaOH titration gives about 85% theoretical. The difference is due to the correction of the sulfate methods for loss on the ion exchange resin. The measured values of 85% of theoretical SO_2 seems reasonable for these low SO_2 concentrations (400 ppm).

The coefficients of variation of the analytical methods at the coal-fired power plant were the same as those for the oil-fired source. Good agreement (correlation coefficients and least squares fits) were obtained for all the methods. The percent theoretical values for SO_2 were 80% for Ba^{++} or Ba Chlor and 73% for NaOH. Again, some of this difference may be due to correction of the sulfate methods for the loss on the ion exchange column.

The SO_3 results from controlled condensation method and the IPA absorption method differ considerably. The correlation coefficients vary from ∿ 0.1 to 0.4. The reason for this is not known at the present time. We suggest that additional testing and laboratory work on these SO_3 collection methods be initiated.

Tests on the effect of NO_x, HCl and organic acids on the wet chemical methods were conducted in the Walden pilot plant. Nitric oxide has no effect on Ba^{++} and NaOH titrations or Ba Chlor even up to a ratio of NO/SO_2 = 3. The NaOH titration is effected by HCl whereas Ba^{++} and Ba Chlor are not. The effect would be most pronounced in low sulfur coals where errors as high as 10 to 20% are possible. Organic acids have no effect on the accuracy of any of the wet chemical methods, however, the endpoint of the NaOH titration is gradual rather than sharp, possibly due to the buffering action of the weak organic acid. The accuracy of the wet chemical methods is estimated as 93 ± 5% based on the pilot plant studies.

SECTION 2

OTHER STATIONARY SOURCES

TABLE OF CONTENTS

Section — Title — Page

2.1 INTRODUCTION 2-1

2.2 GRAY IRON FOUNDRIES 2-2

2.2.1 Brief Description of Foundries 2-2
2.2.2 Sampling and Analytical Results 2-6
2.2.3 Conclusions 2-26

2.3 KRAFT PULPING 2-26

2.3.1 Sources of SO_2 in a Kraft Mill 2-26
2.3.2 Sampling and Analytical Results 2-30
2.3.3 Conclusions 2-39

2.4 IRON AND STEEL 2-40

2.4.1 Brief Description of the Iron and Steel Industry .. 2-40
2.4.2 Sampling and Analytical Results 2-44
2.4.3 Conclusions 2-62

2.5 SMELTING 2-62

2.5.1 Brief Description of Smelting Processes 2-62
2.5.2 Sampling and Analytical Results 2-66
2.5.3 Conclusions 2-83

2.6 SULFURIC ACID PRODUCTION 2-83

2.6.1 Brief Description of Sulfuric Acid Plants 2-83
2.6.2 Sampling and Analytical Results 2-87
2.6.3 Conclusions 2-96

2.7 RECOMMENDATIONS FOR FUTURE WORK 2-96

REFERENCES 2-97

APPENDIX A PROCEDURE FOR SAMPLING AND ANALYSIS A-1

APPENDIX B POTENTIOMETRIC DETERMINATION OF SO_2 IN FLUE GASES WITH AN ION SELECTIVE LEAD ELECTRODE B-1

APPENDIX C SOLID SORBENT STUDIES C-1

APPENDIX D PRECISION OF BARIUM ION TITRATION AND BARIUM CHLORANILATE FOR VARIOUS ANALYSTS D-1

Preceding page blank

LIST OF ILLUSTRATIONS

Figure	Caption	Page
2-1	Sulfur Balance for Gray Iron Foundry	2-7
2-2	Schematic of Gray Iron Foundry	2-8
2-3	Detailed Layout of Gray Iron Foundry Sampling Sites	2-9
2-4	Schematic of Standard and Modified EPA SO_x Sampling Trains	2-15
2-5	Typical Appearance of Particulates and Chemical Map of Fe_4S	2-21
2-6	Rescanning Electron Micrographs	2-22
2-7	Oscilloscope Traces of Si, S and Fe	2-23
2-8	Additional Oscilloscope Traces of Si, S and Fe	2-24
2-9	Typical Flow Diagram for Kraft Pulping	2-28
2-10	Gaseous Sulfur Distribution	2-31
2-11	Schematic of Kraft Mill Operation	2-32
2-12	Detailed Layout of Kraft Mill Sampling Sites	2-34
2-13	Schematic of Coke Oven Site and Sampling Port	2-47
2-14	Sintering Plant Schematic and Test Site	2-48
2-15	Schematic of Open Hearth Unit and Sampling Ports	2-49
2-16	Schematic of the Copper Smelting Operation	2-68
2-17	Duct Cross-Section Showing Probe Penetration (R&R) (Copper Roaster and Reverbatory)	2-69
2-18	Schematic of the Lead Smelting Operation	2-70
2-19	Simplified Flow Diagram of Typical Lead-Chamber Process for Sulfuric Acid Manufacture (Based on Use of Elemental Sulfur as the Raw Material)	2-85
2-20	Gas Flow Diagram for Typical Sulfur-Burning Contact Plant in which Air Quench is Used for Part of Converter Interstage Cooling	2-86
2-21	Sulfuric Acid Plant Layout	2-89

LIST OF TABLES

Table	Title	Page
2-1	Dust and Fume Emissions from Gray Iron Cupolas	2-3

LIST OF TABLES (continued)

Table	Title	Page
2-2	Qualitative Spectrographic Analysis of Two Samples Taken from a Baghouse Serving a Gray Iron Cupola Furnace	2-5
2-3	Supplementary Data for the Gray Iron Foundry	2-10
2-4	SO_2 Test Results from a Gray Iron Foundry	2-11
2-5	Statistical Results for SO_2 Tests from a Gray Iron Foundry	2-17
2-6	Semiquantitative Spectrographic Analysis of an SO_2 Impinger Samples from a Gray Iron Foundry	2-18
2-7	Determination of Trace Metals in SO_2 Impingers from a Gray Iron Foundry by Atomic Absorption Analysis	2-19
2-8	Results of X-Ray Analysis	2-25
2-9	Characteristics of Kraft Pulping	2-27
2-10	SO_2 Emissions from Kraft Pulping Process	2-29
2-11	SO_2 Test Results from a Pulp and Paper Mill	2-35
2-12	Supplementary Data from the Pulp and Paper Mill	2-38
2-13	Emissions of Sulfur Oxides to the Atmosphere from the Iron and Steel Industry (1967)	2-41
2-14	Composition of Coke Oven Gas	2-42
2-15	Supplementary Data from the Iron and Steel Plant	2-46
2-16	SO_2 Test Results from an Iron and Steel Plant (Coke Oven)	2-50
2-17	SO_2 Test Results from an Iron and Steel Plant (Coke Oven)	2-52
2-18	SO_2 Test Results from an Iron and Steel Plant (Sinterer) .	2-53
2-19	SO_2 Test Results from an Iron and Steel Plant (Open Hearth)	2-55
2-20	Statistical Analysis for SO_2 Test Results from an Iron and Steel Plant	2-56
2-21	Semiquantitative Spectrographic Analysis of an SO_2 Impinger Sample from an Iron and Steel Plant (Coke Oven) ...	2-57
2-22	Sulfur Balance for Coke Oven Operation (Based on Production of One Net Ton of Coke)	2-59
2-23	Sulfur Balance for Sintering Machine Operation (Based on the Production of One Net Ton of Sinter)	2-61
2-24	Sulfur Dioxide Emissions	2-64

LIST OF TABLES (continued)

Table	Title	Page
2-25	SO_2 Test Results from a Copper Smelter (Roasting and Reverberatory)	2-71
2-26	Supplementary Data for the Copper and Lead Smelters	2-73
2-27	SO_2 Test Results from a Lead Smelter	2-74
2-28	Statistical Analysis for SO_2 Test Results from Smelters	2-76
2-29	Semiquantitative Emission Spectrographic Analysis of SO_2 Impinger Samples from Smelting Operations	2-77
2-30	Atomic Absorption Results from Analysis of SO_2 Impinger Liquid from Copper and Lead Smelting	2-78
2-31	SO_3 Test Results from Cu and Pb Smelting Operations	2-80
2-32	Log of Operations for Copper and Lead Smelters	2-82
2-33	Collection of H_2SO_4 Mist from a Sulfur-Burning Contact Sulfuric Acid Plant with Fiber Mist Eliminators	2-88
2-34	SO_2 and SO_3 Test Results from a Sulfuric Acid Plant	2-90
2-35	SO_2 and SO_3 Test Results from a Sulfuric Acid Plant	2-95

2.1 INTRODUCTION

The second phase of this program was started in November 1971 with additional funds from EPA. The purpose of this portion of the program was to investigate the feasibility of using SO_x methods (developed for sampling and analysis of fossil fuel combustion effluents) in other industries including some Category II sources. These included:

Gray iron foundries
Kraft pulping
Iron and steel
Smelting
Sulfuric acid production

The program plan was to run the EPA procedure, evaluate the data, and repeat with modification of the sampling and/or analytical procedures as required.

The SO_2 samples were analyzed by three different analytical procedures. Each was subject to different interferences. For example, the two sulfate specific methods were Ba^{++} and barium chloranilate which have interferences from sodium and potassium (Ba^{++}) ions, or zinc, calcium, lead (Ba Chlor) ions, respectively. The NaOH titration does not have any interferences from metals, however, carbonates, oxides or other basic and strongly acidic species will interfere.

For any source sampled, one could decide whether modifications were required on a statistical basis. For example, if high correlation coefficients with least squares slopes near unity were obtained after intercomparison of all the methods, we assumed that no interferences were present since each method has its own characteristic interference.

Early in the evaluation program, we found that a modification to the sampling train in the field (inclusion of a fine particulate filter) eliminated the necessity for changes to the analytical methods which could improve accuracy or precision. The majority of the tests, therefore, were conducted with and without the fine particulate filter to determine the effect of interferences on the methods. Following statistical analysis of the data, we could determine whether any modifications to the original EPA method were required.

In the following sections, we discuss, for each source, the characteristics, the sampling and analytical methods including test data, and the conclusions and recommendations.

2.2 GRAY IRON FOUNDRIES

2.2.1 Brief Description of Foundries

Gray iron foundries produce metal castings from melted scrap metal such as automobile parts, pig iron, etc. A number of different types of furnaces are used in the ferrous and non-ferrous foundry industry each having a special application and a characteristic contribution to atmospheric pollution.

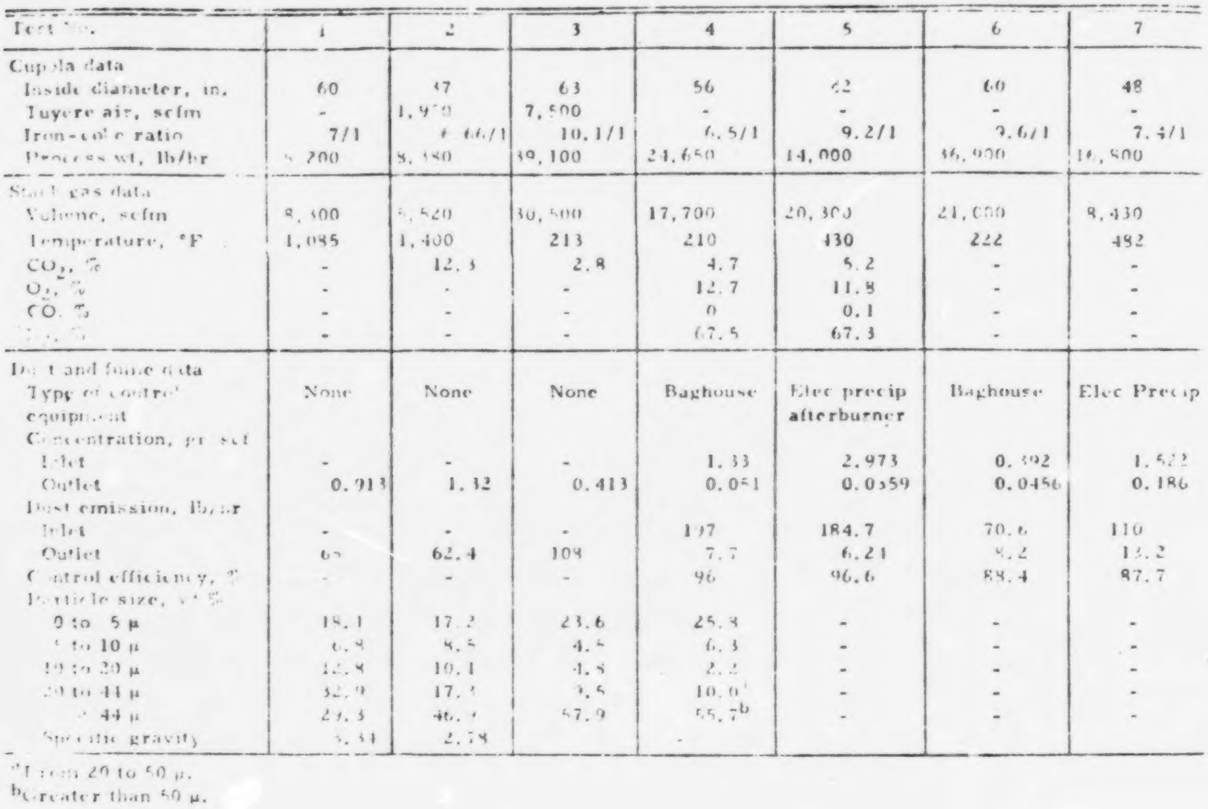
Of the numerous types of furnaces, the cupola is the one most commonly used. Approximately 90% of the gray iron melting furnaces are cupolas and only 15 to 18% of these have air pollution control devices installed (Giever, 1970).

One of the important characteristics of cupola effluent is the temperature. This is a factor to consider in the design of control equipment and has been one of the primary problems in the collection of satisfactory data on other characteristics of the effluent. The temperature of the effluent has been found to exceed 2000°F in some instances. This high temperature not only hampers evaluation but presents special problems of control that are difficult to attain, costly to install, and expensive to maintain. Cupola effluents, when uncontrolled, may be generally characterized as consisting of large quantities of solid particles, dark, often oily smoke, gas and fumes released to the atmosphere at temperatures often too high to permit the standard types of stack effluent evaluation.

Cupolas without air pollution control devices are reported to emit an average of 17 pounds of particulates per ton of iron melted based on 20 tons/hour production (Giever, 1970). Some characteristic emission data on cupolas is given in Table 2-1.

TABLE 2-1

DUST AND FUME EMISSIONS FROM GRAY IRON CUPOLAS



Test No.	1	2	3	4	5	6	7
Cupola data							
Inside diameter, in.	60	37	63	56	42	60	48
Tuyere air, scfm	-	1,970	7,500	-	-	-	-
Iron-coke ratio	7/1	4.66/1	10.1/1	6.5/1	9.2/1	9.6/1	7.4/1
Process wt, lb/hr	8,200	8,380	39,100	24,650	14,000	36,900	16,800
Stack gas data							
Volume, scfm	8,300	5,520	30,500	17,700	20,300	21,000	8,430
Temperature, °F	1,085	1,400	213	210	430	222	482
CO_2, %	-	12.3	2.8	4.7	5.2	-	-
O_2, %	-	-	-	12.7	11.8	-	-
CO, %	-	-	-	0	0.1	-	-
N_2, %	-	-	-	67.5	67.3	-	-
Dust and fume data							
Type of control equipment	None	None	None	Baghouse	Elec precip afterburner	Baghouse	Elec Precip
Concentration, gr/scf							
Inlet	-	-	-	1.33	2.973	0.392	1.522
Outlet	0.913	1.32	0.413	0.051	0.0359	0.0456	0.186
Dust emission, lb/hr							
Inlet	-	-	-	197	184.7	70.6	110
Outlet	65	62.4	108	7.7	6.21	8.2	13.2
Control efficiency, %	-	-	-	96	96.6	88.4	87.7
Particle size, wt %							
0 to 5 μ	18.1	17.2	23.6	25.8	-	-	-
5 to 10 μ	6.8	8.5	4.5	6.3	-	-	-
10 to 20 μ	12.8	10.1	4.8	2.2	-	-	-
20 to 44 μ	32.9	17.3	9.5	10.0[a]	-	-	-
> 44 μ	29.3	46.9	57.9	55.7[b]	-	-	-
Specific gravity	3.34	2.78		-			

[a] From 20 to 50 μ.

[b] Greater than 50 μ.

From J. A. Danielson, Air Pollution Engineering Manual, U.S. Dept. HEW, Pub. No. 999-AP40 (1967).

Particulate material emitted from the collectors will be composed of coke, limestone, foreign particles associated with the scrap along with metallic oxides, fumes and sulfides. Additional data on the metallic element composition of cupola emissions collected in a baghouse is shown in Table 2-2.

A study of foundry cupolas in the Los Angeles area (Danielson, 1967) showed up to *24% by weight of the solids were below 10μ.* It was also reported that 74% of the total weight was greater than 325 mesh. Particles of 1/4 to 3/8 inches in diameter may be blown from the stack of an uncontrolled cupola from the blowdown operation.

In addition to particulate matter, the effluent from cupolas contains gases which are primarily carbon dioxide and nitrogen with some excess oxygen and varying amounts of sulfur dioxide, carbon monoxide and hydrocarbons.

Most states have recently adopted regulations requiring stringent control of cupola particulate emissions. Once these regulations become effective, generally by 1974-75, the sampling environment in the effluent gas stream will change greatly. The two most commonly employed control techniques used in foundries are wet scrubbers (venturi) and baghouses. In both the exit gases will be at considerably lower temperatures than are characteristic of the uncontrolled top gases. The contact with water in the scrubber inherently produces cooling, with accompanying saturation of the gases. In order to prevent damage to the filter materials, the top gases are cooled prior to entering the baghouse in a water quench step.

The final effluent stream will probably be free of carbon monoxide, unlike the top gases where carbon monoxide levels can reach 15% or more. An afterburner in which the carbon monoxide is oxidized to carbon dioxide is usually installed to reduce the explosion hazard and to control monoxide emissions to the atmosphere. The afterburner can be installed either in front of or behind the particulate control unit.

The primary source of sulfur in these operations is from the coke charge. Coke of 0.6% sulfur could result in the emission of 1.6 to 2.5

TABLE 2-2

QUALITATIVE SPECTROGRAPHIC ANALYSIS OF TWO SAMPLES TAKEN FROM A BAGHOUSE SERVING A GRAY IRON CUPOLA FURNACE[a]

Element	Approx amount, %	Approx amount, %
	Sample A	Sample B
Aluminum	0.81	1.1
Antimony	0.24	0.24
Boron	0.050	0.054
Cadmium	0.13	0.064
Calcium	0.16	0.25
Chromium	0.022	0.019
Copper	0.42	0.32
Gallium	0.017	0.019
Germanium	0.018	0.015
Iron	6.0	7.5
Lead	17.0	17.0
Magnesium	0.29	0.30
Manganese	1.0	0.81
Molybdenum	0.0068	0.0075
Nickel	0.023	0.022
Potassium	1.5	1.2
Silicon	8.6	15.0
Silver	0.0093	0.0089
Tin	0.41	0.38
Titanium	0.019	0.034
Zinc	7.1	5.9

[a] These data are qualitative only and require supplementary quantitative analysis for actual amounts of the elements found to be present. These are the same samples as given in Table 77.

[a] These data are qualitative only and require supplementary quantitative analysis for actual amounts of the elements found to be present.

From J. A. Danielson, Air Pollution Engineering Manual, U.S. Dept. HEW, Pub. No. 999-AP40 (1967).

pounds of SO_2 per ton of melt. The concentration of SO_2 (if all the sulfur in the coke goes into the gas stream) in the top gases is 300 to 470 ppm based on an average quantity of gas of 35,000 scf per ton of melt (Environmental Engineering, 1971). It should be noted, however, that 60,000 scf per ton of melt is a more reasonable estimate. On the basis of a larger gas volume, the estimated SO_2 concentration would be 200-300 ppm. A sulfur balance on foundries is shown in Figure 2-1. The data of Cowan (1971) indicates only ∿ 20-40 ppm of SO_x in the effluent. Cowan's SO_2 value is considerably lower than that estimated by Environmental Engineering (1971). The reason for this difference is discussed in some detail in the following section.

2.2.2 Sampling and Analytical Results

Two different locations were selected for sampling at the gray iron foundry. These are shown in Figure 2-2. A detailed layout of the sampling sites is given in Figure 2-3. The wet scrubber is typical of a control system used on a foundry. (The liquid in the high pressure-drop venturi scrubber is water.) Some supplementary data for the foundry is given in Table 2-3. A few SO_2 tests were run at the scrubber outlet. The sampling system was the conventional EPA SO_x train with no modifications (Federal Register, 1971). The first five runs in Table 2-4 were taken at the outlet of the high pressure drop (35" H_2O) venturi scrubber. Two trains were run in parallel off the same probe. These are reported as runs A and B in Table 2-3. The sampling rate for each train was about 3 liters/min for a 20-30 minute period. The major problem encountered in sampling was that the glass wool filter in the probe became plugged. *The glass wool had to be replaced after each run.* In addition, a large amount of the particulate matter was carried into the impingers. The glass wool filter (plug) in the probe proved to be *ineffective* for removing the particulate matter from foundry effluent (see previous data on particle size section).

Before the impinger samples could be analyzed in the laboratory, the particulate matter had to be removed by filtration through a 0.45μ Millipore cellulose acetate filter. Due to the low SO_2 levels (runs 1-5), the samples were analyzed by the barium ion titration only.

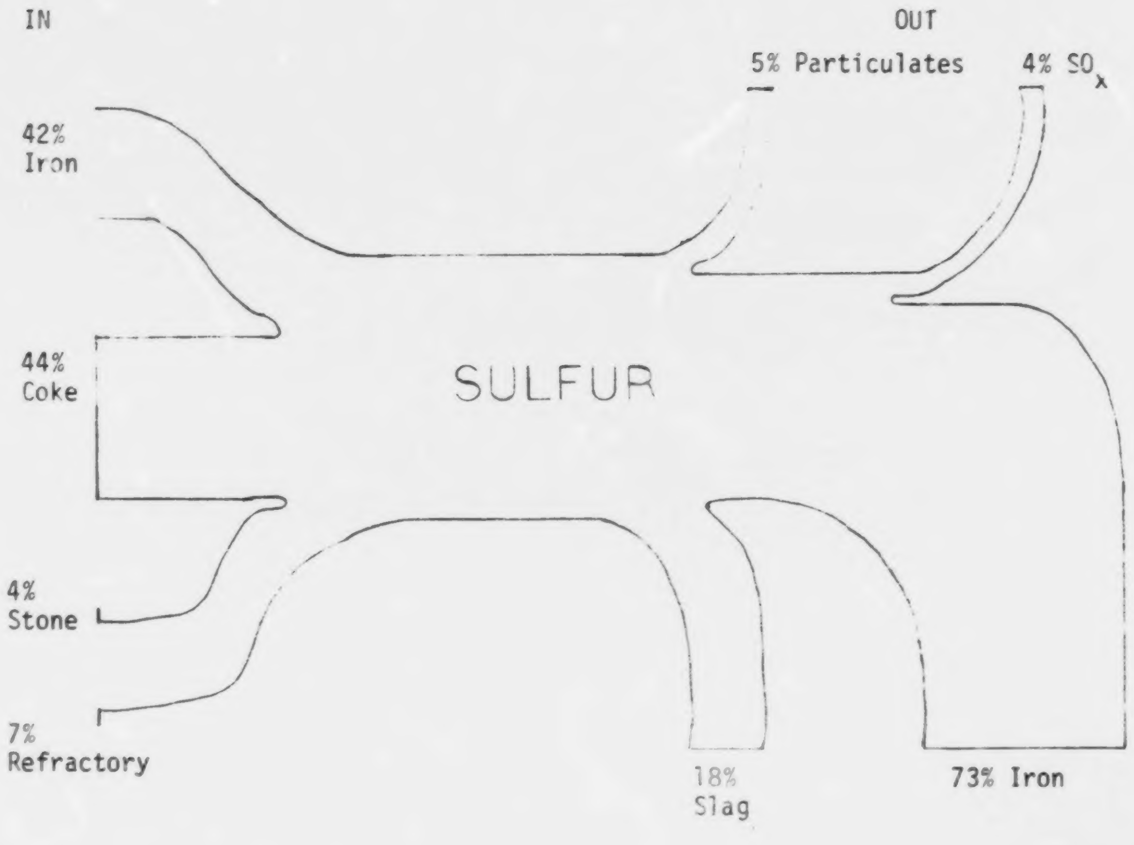

IN
OUT
5% Particulates
4% SO_x
42% Iron
44% Coke
SULFUR
4% Stone
7% Refractory
18% Slag
73% Iron

Figure 2-1. Sulfur Balance for Gray Iron Foundry.

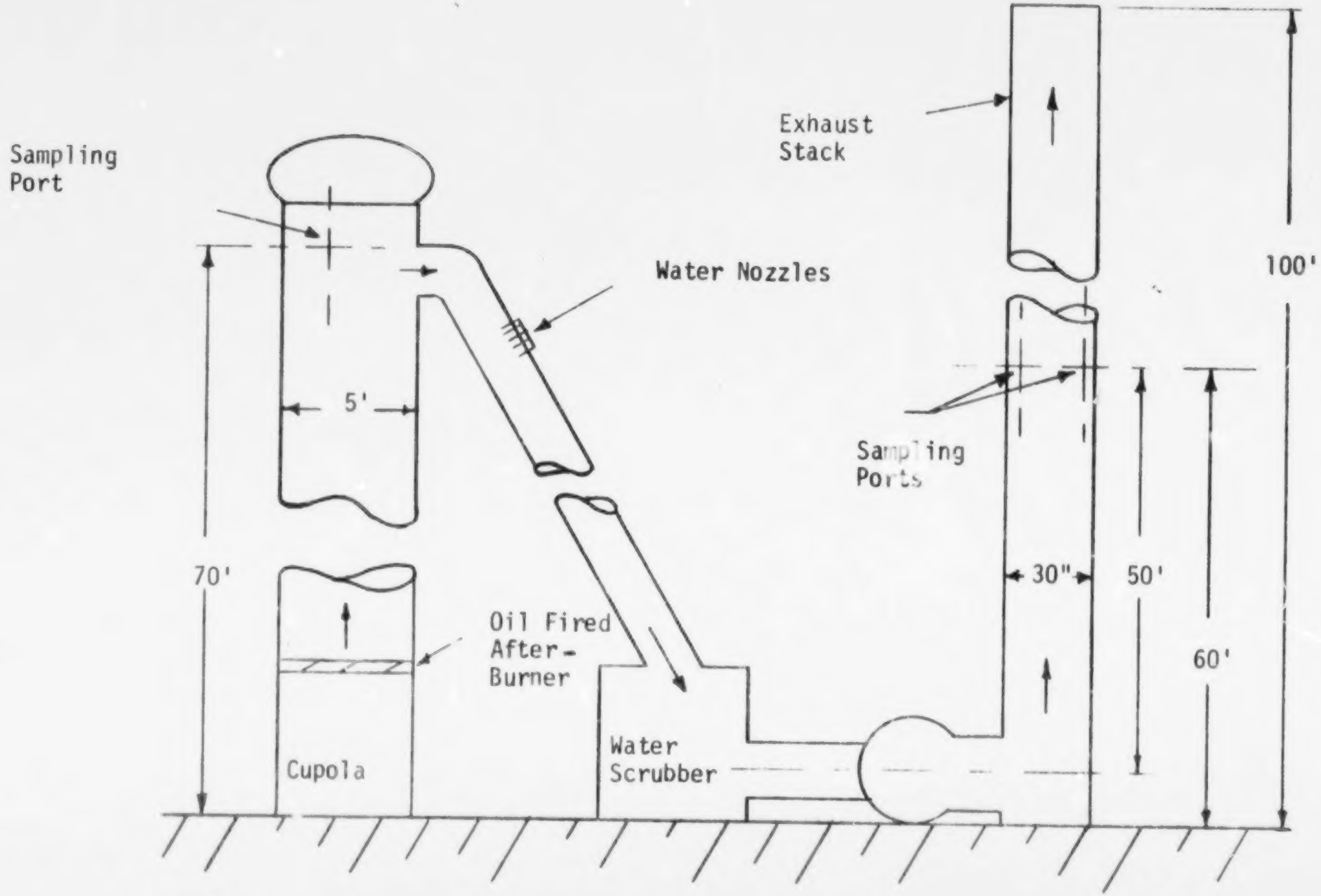

Sampling
Port
Water Nozzles
Exhaust
Stack
100'
5'
Sampling
Ports
70'
30"
50'
60'
Oil Fired
After-
Burner
Cupola
Water
Scrubber

Figure 2-2. Schematic of Gray Iron Foundry.

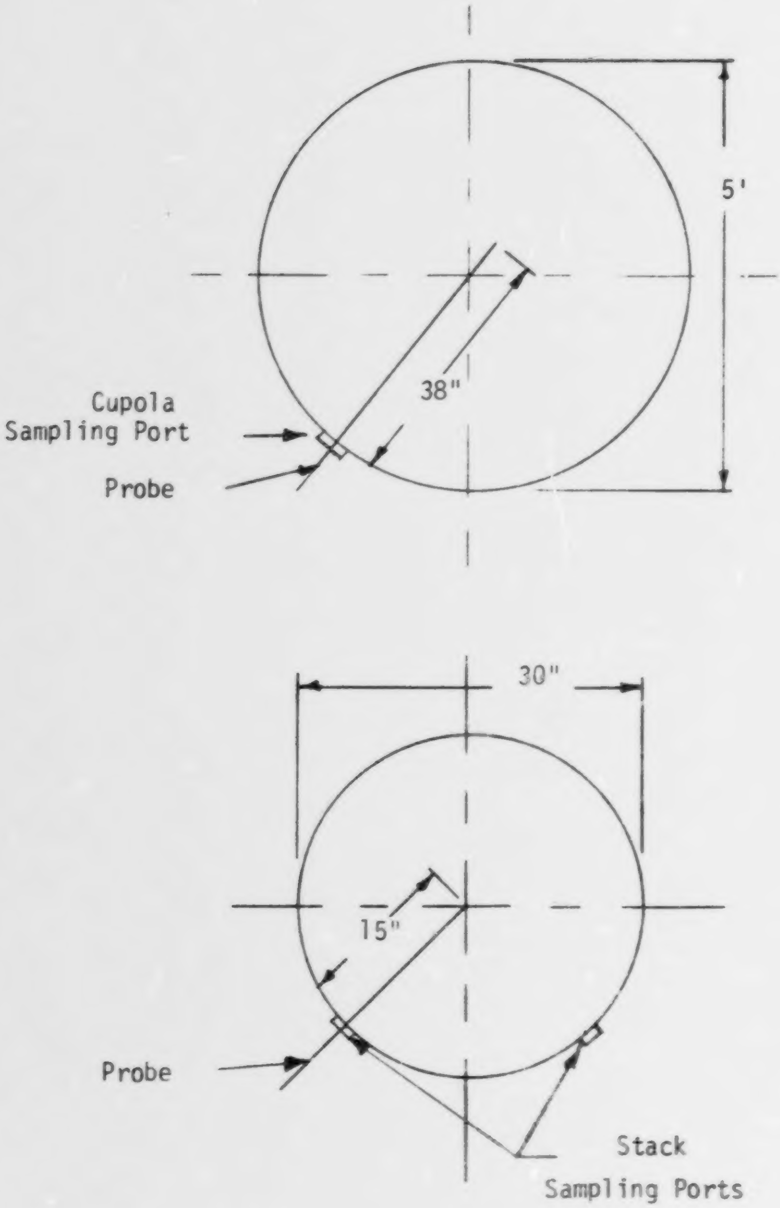

5'
Cupola
Sampling Port
38"
Probe
30"
15"
Probe
Stack
Sampling Ports

Figure 2-3. Detailed Layout of Gray Iron Foundry Sampling Sites.

TABLE 2-3

SUPPLEMENTARY DATA FOR THE GRAY IRON FOUNDRY

Run No.	Date	Sampling Location	% CO_2	% O_2
1-3	11/15/71	Scrubber Outlet*	13.0	3.3
4-5	11/16/71	Scrubber Outlet	14.2	3.8
6-8	11/19/71	Hot Stack+	16.2	0.5
9-11	11/23/71	Hot Stack	16.2	1.8
12-15	11/24/71	Hot Stack	15.5	0.5
16-20	11/29/71	Hot Stack	15.2	0.4
21-24	11/30/71	Hot Stack	16.8	0.5
25-27	12/1/71	Hot Stack	15.6	0.0
28-33	12/2/71	Hot Stack	15.0	0.5
34-36	12/3/71	Hot Stack	15.8	0.5
70-76	1/12/72	Hot Stack	--	--
77-84	1/13/72	Hot Stack	--	--

---

*Stack temperature = 160°F

+Stack temperature = 300°F early morning, >1500°F midafternoon.

TABLE 2-4

SO_2 TEST RESULTS FROM A GRAY IRON FOUNDRY

Sample No.	ppm SO_2 †† (NaOH)	ppm SO_2 †† (Ba^{++})	ppm SO_2 †† (Ba Chlor)
1A†		7	
1B†		5	
2B		22	
3A		22	
3B		12	
4A		18	
4B		55	
5A		41	
5B		50	
6A	27	71	87
6B	32	55	55
7A	46	82	77
7B	46	76	81
8A	0	0	32
8B	0	20	18
9A	96	130	169
9B	84	112	157
10A	68	94	147
10B	51	75	169
11A	78	116	186
11B	No endpoint	92	182
12A		128	133
12B		142	71
13A		42	18
13B		34	23
14A		76	77
14B		73	78
15A		32	42
15B		34	51
16A		123	125
16B		122	115
17A		9	9
17B		10	10
18A		14	17
18B		16	17
19A		92	103
19B		90	158
20A		0	0
20B		118	221
21A		89	183
21B		102	226
22A		6	15
22B		6	19

TABLE 2-4 (continued)

Sample No.	ppm SO_2†† (NaOH)	ppm SO_2†† (Ba^{++})	ppm SO_2†† (Ba Chlor)
23A		10	11
23B		10	13
24A		31	152
24B		36	89
25A		4	23
25B		4	3
26A		33	65
26B		34	39
27A		110	118
27B		118	127
28A		70	76
28B		43	49
29A		101	228
29B		60	144
30A		201	377
30B		84	101
31B		82	198
32A		43	52
32B		44	56
33A		88	86
34A		19	14
34B		22	17
35A		6	7
35B		18	13
36A		83	60
36B		70	89
70A*		203	201
70B*		183	171
71A*		76	57
71B*		76	59
72A*	47	51	51
72B*	54	53	39
73A*	94	78	69
73B*	89	77	67
74A*	26	28	19
74B*	26	27	20
75A*	48	43	31
75B*	53	47	35
76A*	45	54	37
76B*	41	51	42
77A*	25	19	17
77B*	32	23	19
78A*	39	25	19
78B*	43	25	19
79A*	56	34	27
79B*	63	38	28

TABLE 2-4 (continued)

Sample No.	ppm SO_2 [††] (NaOH)	ppm SO_2 [††] (Ba^{++})	ppm SO_2 [††] (Ba Chlor)
80A*	64	65	57
80B*	69	71	63
81A*	38	34	19
81B*	40	34	27
82A*	83	57	50
82B*	84	61	55
83A*	125	109	105
83B*	143	125	119
84A*	42	41	47
84B*	39	40	29

---

[*] with fine particulate filter

[†] A and B represent results from two parallel trains run off the same probe.

[††] These analytical methods (NaOH, Ba^{++}, Ba Chlor) were run on aliquots of the same sample.

The sample train modification necessary for sampling the hot (cupola) stack involved replacement of the pyrex liner with a *vycor* probe liner since the stack temperatures were generally in excess of 1500°F. Tests 6 to 11 were analyzed by all three methods. The NaOH titration gave low results due presumably to the presence of basic components (metal oxides, metal carbonates, etc.) in the flue gas. This method was discontinued after run 11.

The SO_3 results* obtained by absorption in 80% isopropanol-20% water were very low and ranged from about 2-5 ppm by either the barium ion titration or barium chloranilate methods.

The color change in the barium ion titration method was very unusual for samples 6-8 in that a green color was observed when the indicator was added and the titration endpoint was pale yellow. The barium ion titration endpoints for the remaining runs (9-36) had the normal color change *but were very difficult to detect.*

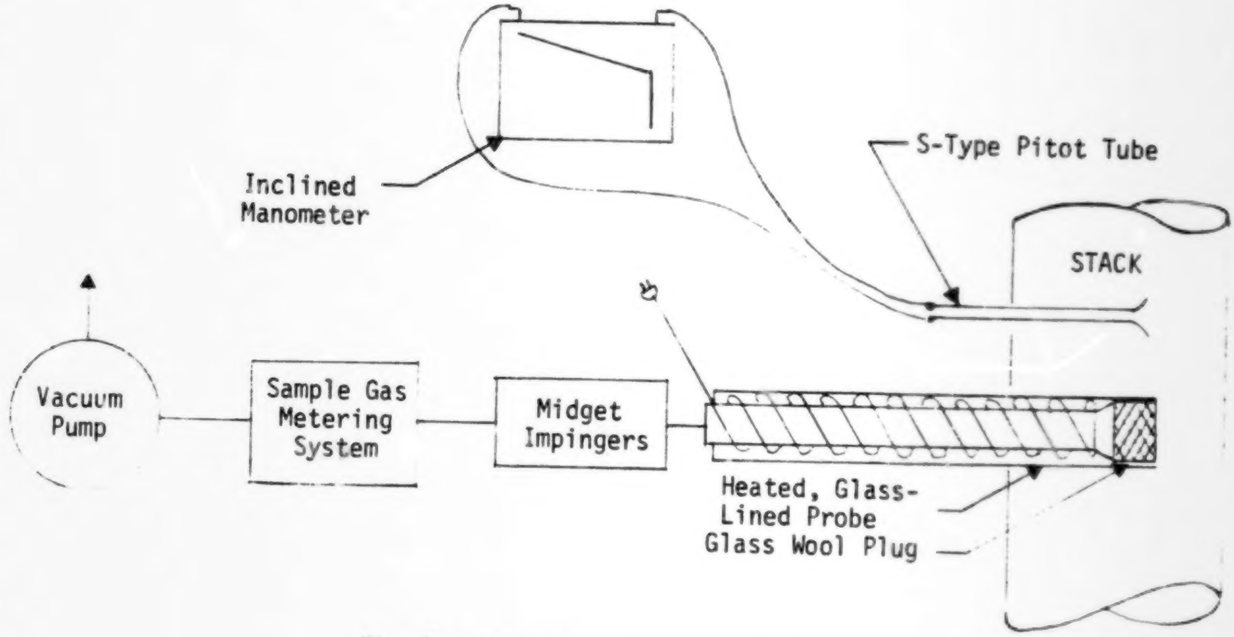
The barium chloranilate method gave considerably higher results for SO_2 than the barium ion titration for runs 6-36. The average SO_2 concentration (runs 4-36) was 90 ppm (Ba Chlor) versus 57 ppm for runs 1-36 by barium titration.

Since we obtained considerably different SO_2 results by analysis of aliquots of the impinger samples with two methods each specific for sulfate, we decided to modify the sampling train. We anticipated that the problem could be eliminated by reducing the quantity of particulate matter reaching the impingers. This would be true *only* if the reactions leading to poor precision and accuracy occurred in the condensed phase (in the impinger).

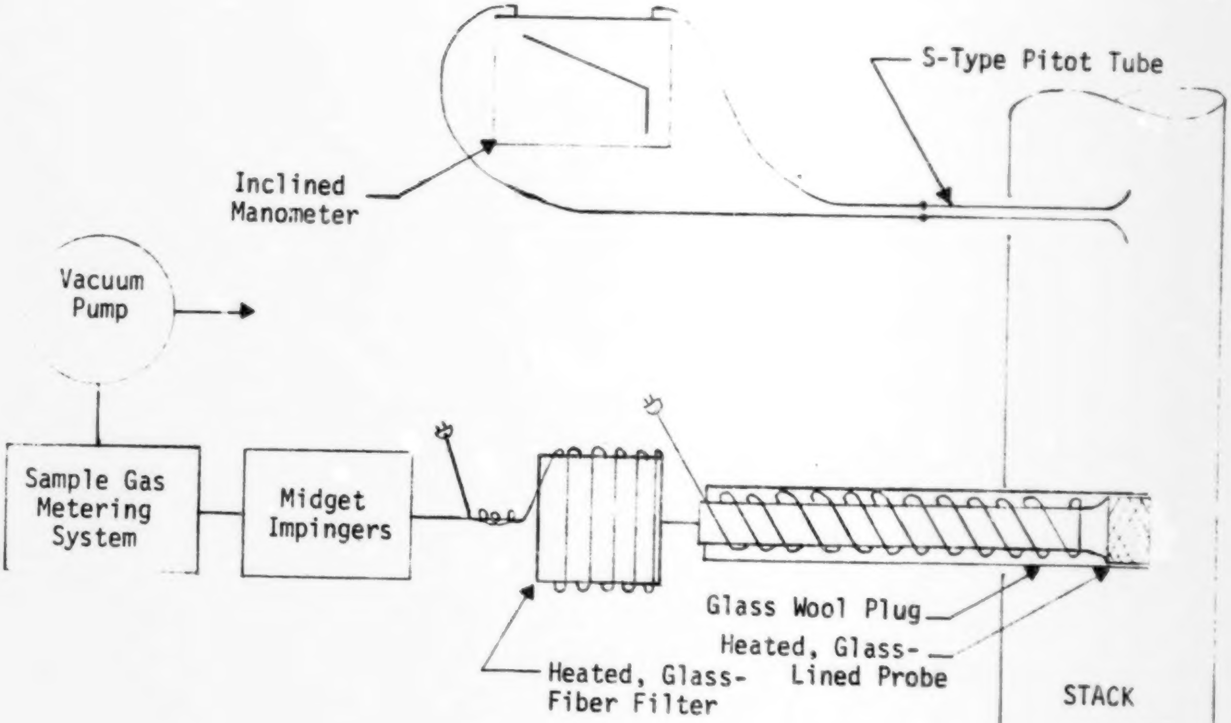
The SO_2 train was modified by placing a heated high efficiency (0.3μ) glass fiber filter between the probe and the first impinger. The two trains are shown in Figure 2-4. The results (runs 70-84) are given in

---

*The condenser was not used because of problems (plugging) expected with the high particulate loadings.


S-Type Pitot Tube
Inclined Manometer
STACK
Vacuum Pump
Sample Gas Metering System
Midget Impingers
Heated, Glass-Lined Probe
Glass Wool Plug

Standard EPA SO_x Sampling Train


S-Type Pitot Tube
Inclined Manometer
Vacuum Pump
Sample Gas Metering System
Midget Impingers
Glass Wool Plug
Heated, Glass-Lined Probe
Heated, Glass-Fiber Filter
STACK

Modified EPA SO_x Sampling Train

Figure 2-4

Table 2-4. With this modification, the agreement between the barium chloranilate and barium ion titration methods is excellent. Note that even the NaOH titration yields results which agree well with the methods specific for sulfate. The color change associated with the barium ion titration *was extremely sharp and considerably improved.* The endpoint change was even clearer (at these low SO_2 levels) than that obtained at other sources where no filter had been used. The problematic endpoint occasionally noted in the titration for this method may be due to trace metallic impurities.

Statistical analysis of the results from Table 2-4 is shown in Table 2-5. The improvement is clearly demonstrated by the higher correlation coefficients and regression equations with slopes close to unity for the filtered samples. The change in the CV for these methods is quite drastic. Samples of the impinger liquid (filtered and unfiltered) were analyzed by emission spectroscopy. The semi-quantitative results are given in Table 2-6. The large CV's (poor precision) for barium chloranilate are due to the high concentrations of metallic species such as Zn, Pb, Ca which are known interferences. In the unfiltered samples the sum of the concentrations of the metallic species is approximately equal to the SO_2 concentration. The CV of the filtered sample analyzed by barium chloranilate is still high for this concentration (3-5% would be expected if no interference were present). The traces of Zn and Ca still found in the samples may be responsible for this. The interference in the barium ion titration method is not quite as severe as the barium chloranilate but there is a marked difference between filtered and unfiltered samples. A scan of the data in Table 2-6 indicates that the high Na levels which are reduced with filtration may be the interference. This is confirmed by the data in Table 2-7 which shows that the Na concentration is 4-5 times the SO_2 concentration. The reduction in the concentration of Na by the fine particulate filter is responsible for the improved CV of the Ba^{++} titration. Note that the CV of the filtered sample is only slightly higher than found for combustion sources if no interference were present. The NaOH titration which has no metal ion interferences has excellent precision and agreement with the sulfate methods once the metal oxides or carbonates are removed by the fine particulate filter.

TABLE 2-5

STATISTICAL RESULTS FOR SO_2 TESTS FROM A GRAY IRON FOUNDRY

Run No.	Regression Equation	Correlation Coefficient	Coefficient of Variation of Analytical Method	Mean SO_2 Conc. (ppm)	Remarks
1-36	ppm SO_2 (Ba Chlor) = -3.63 + 1.54 ppm SO_2 (Ba^{++})	0.826			With glass wool filter only
1-36			Ba^{++} titr. = 11%	57	
4-36			Ba Chlor = 27%	90	
70-84	ppm SO_2 (Ba^{++}) = -8.84 + 1.09 ppm SO_2 (Ba Chlor)	0.993			With heated fine particulate filter and glass wool filter
	ppm SO_2 (Ba^{++}) = 3.68 + 1.08 ppm SO_2 (NaOH)	0.938			
	ppm SO_2 (NaOH) = 1.06 ppm SO_2 (Ba Chlor) + 12.9	0.930	Ba^{++} titr. = 3.4%	62	
			Ba Chlor = 8.8%	53	
			NaOH titr. = 0.3%	58	

TABLE 2-6

SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSIS OF AN SO_2 IMPINGER SAMPLES FROM A GRAY IRON FOUNDRY

	ppm Al	ppm B	ppm Be	ppm Cu	ppm Cr	ppm Fe	ppm Mg	ppm Mn	ppm Ni
Just glass wool filter	1-10	0.03-0.3	--	0.3-3	0.03-0.3	3-30	1-10	0.3-3	0.01-0.1
With additional fine particulate filter	0.1-1	0.1-1	0.001-0.01	0.3-3	0.01-0.1	0.3-3	0.1-1	0.01-0.1	0.003-0.03

	ppm Ag	ppm Pb	ppm Sn	ppm Ca	ppm Si	ppm Ti	ppm Zn	ppm Na
Just glass wool filter	0.3-3	3-30	0.03-0.3	1-10	0.3-3	0.01-0.1	3-30	3-30
With additional fine particulate filter	0.1-1	0.1-1	--	0.3-3	0.1-1	0.003-0.03	0.03-0.3	1-10

TABLE 2-7

DETERMINATION OF TRACE METALS IN SO_2 IMPINGERS FROM A GRAY IRON FOUNDRY BY ATOMIC ABSORPTION ANALYSIS

	ppm					
Sample	Na	Zn	Ca	Pb*	Cu*	Remarks
A	210	19	14	20	0.3	Without fine particulate filter
B	240	3.0*	10	BD	0.3	Without fine particulate filter
C	8.5	0.7*	BD	BD	0.3	With fine particulate filter
D	7.7	0.5*	BD	BD	0.3	With fine particulate filter
E	BD	0.5*	BD	BD	BD	With fine particulate filter

---

*Quantitative emission spectroscopy

BD = Below Detectable = 3.6 ppm for Na and Ca by AA
= 3.0 ppm for quantitative emission spectroscopy for Pb

Some samples of particulate which was removed by filtration from the SO_2 samples 1-36 were sent to the Environmental Protection Agency for electron microprobe analysis. The results are shown in Figures 2-5 to 2-8. There was a considerable difference in the particulate loading which was reflected in the intensity of the sulfur emission line (oscilloscope traces). The sulfur X-ray scans show only a general distribution of sulfur throughout the sample. The apparent higher concentration of sulfur across the filter is due to severe topographical unevenness. The elements present in the particulate matter are given in Table 2-8. *It is interesting to note that sulfur is the primary element in the particulate matter.*

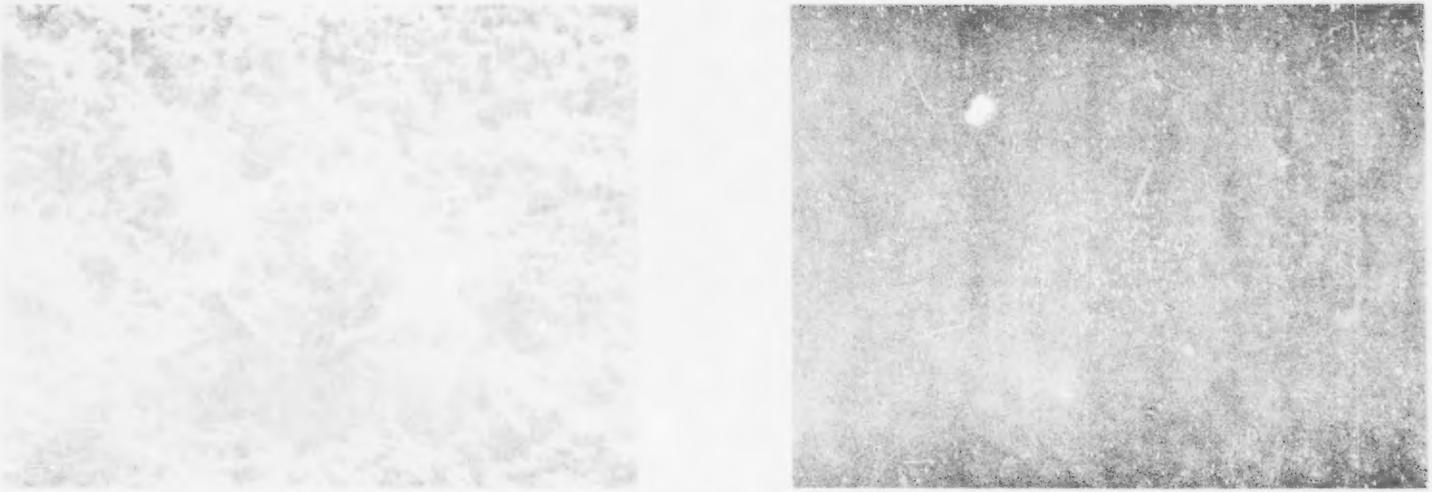
Environmental Engineering (1971) predict SO_2 concentrations of 300-470 ppm if all the sulfur in the coke were emitted as SO_2. The material balance of sulfur in foundries by Cowan (1971) (see Figure 2-1) predicts that about 10% of the sulfur in the coke is emitted as gaseous SO_x. Cowan indicates that a considerable amount (5%) of sulfur is retained in the particulate matter. The majority of the sulfur ends up in the molten iron (see Figure 2-1) and that 20-40 ppm of sulfur oxides are present in the effluent. The average of the "filtered" samples is about 60 ppm. The slightly higher SO_2 values may be the result of the charge in this particular foundry. Automobile engine blocks are the major starting material. These are quite oily and the low but significant sulfur content of the lubricating oil may account for this difference. The agreement with Cowan's predictions is quite encouraging.

Ryason and Harkins (1967) have studied a method for reducing SO_2 to sulfur with carbon monoxide according to the following reaction:

$$2CO + SO_2 \rightarrow 2CO_2 + \frac{1}{2} S_2$$

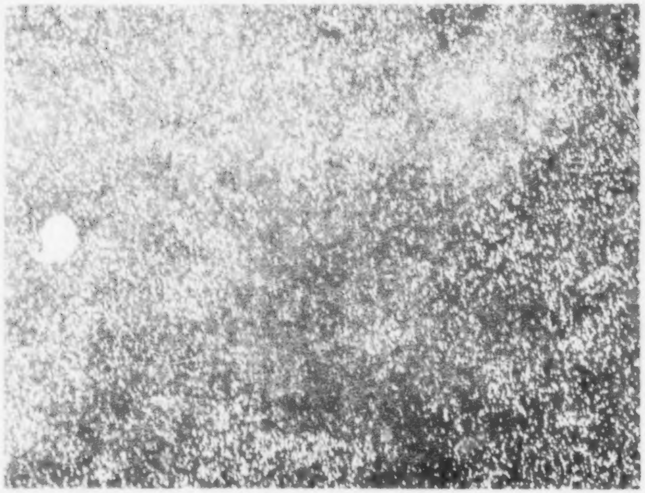
This reaction may account for the elemental sulfur found in the particulate matter by electron microprobe analysis. If CO is present at > two times the SO_2 level, COS could be formed by the reaction:

$$CO + \frac{1}{2} S_2 \rightarrow COS$$



Scanning Electron Micrograph of
Particulate Material From Iron Smelter
Cupola. Filter #30A
Magnification 950X

Fe X-Ray Scan of Area Shown
In Micrograph

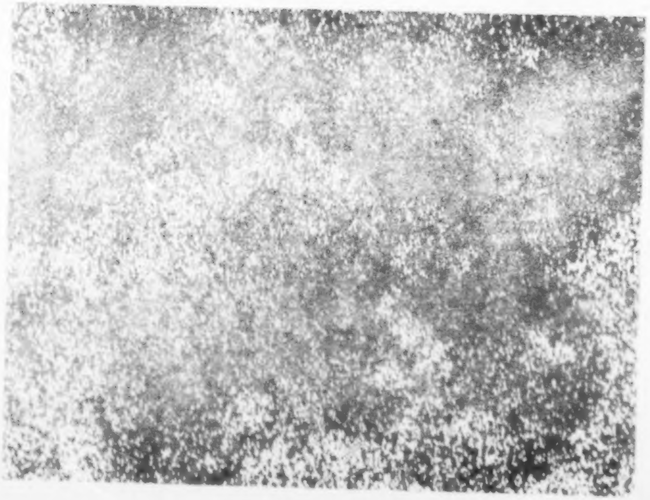


Sulfur X-Ray Scan from Area in Micrograph

Figure 2-5. Typical Appearance of Particulates and Chemical Map of Fe_4S.

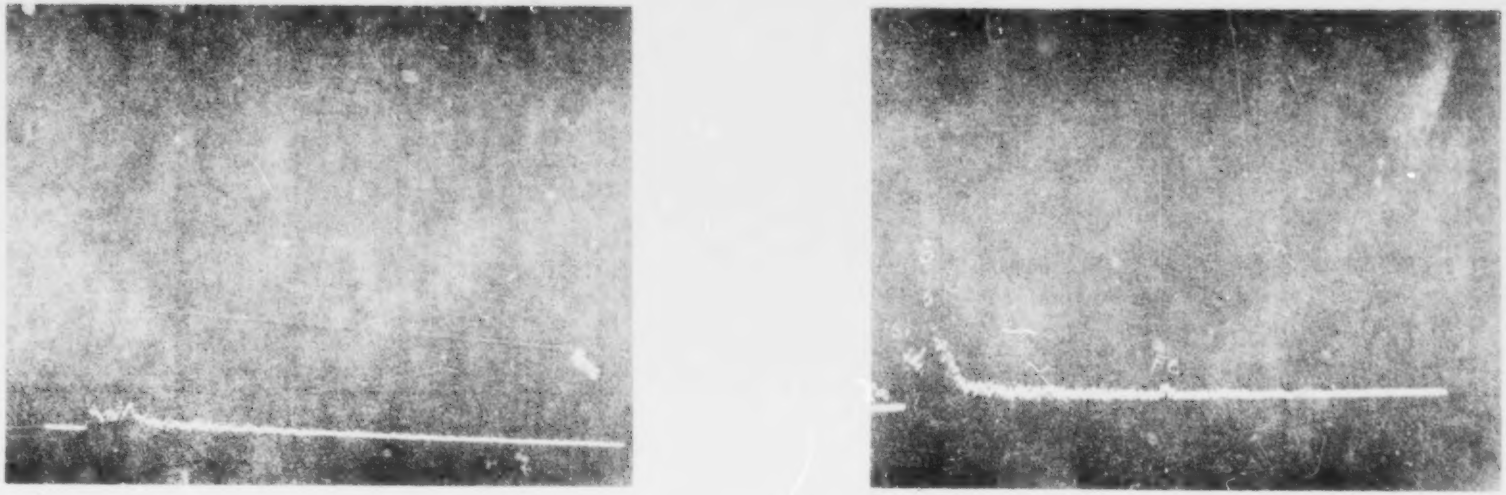
Scanning Micrograph of Particulates on Filter 30A

Fe X-Ray Scan of Area in Micrograph



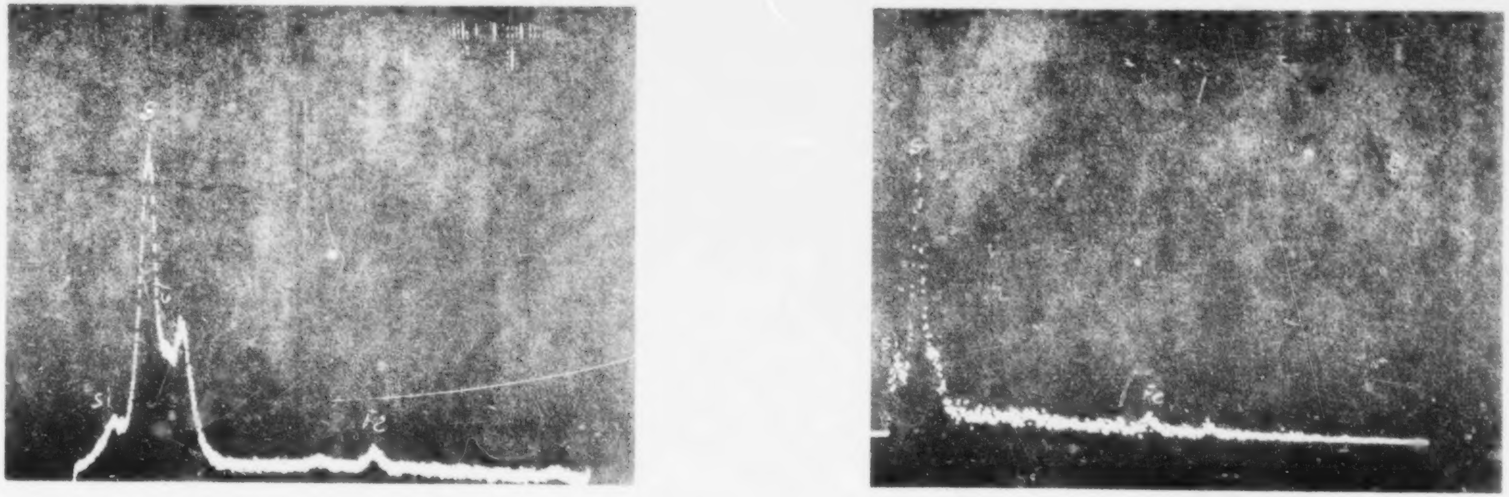
Sulfur X-ray Scan of Area in Micrograph

Figure 2-6. Rescanning Electron Micrographs.



EDX Oscilloscope Trace From Blank

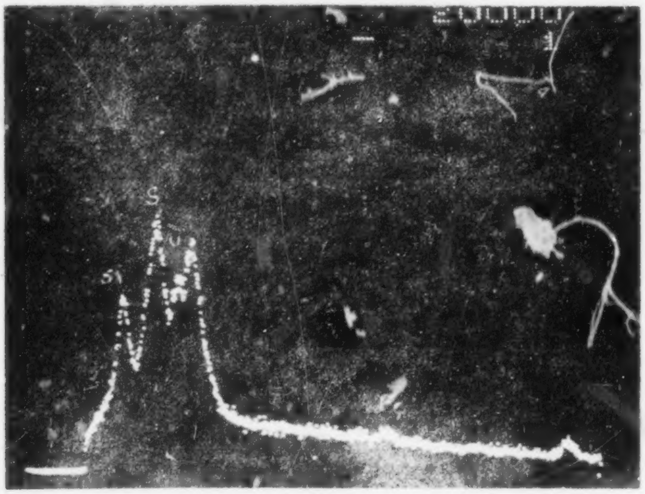
EDX Oscilloscope Trace from Filter 14A



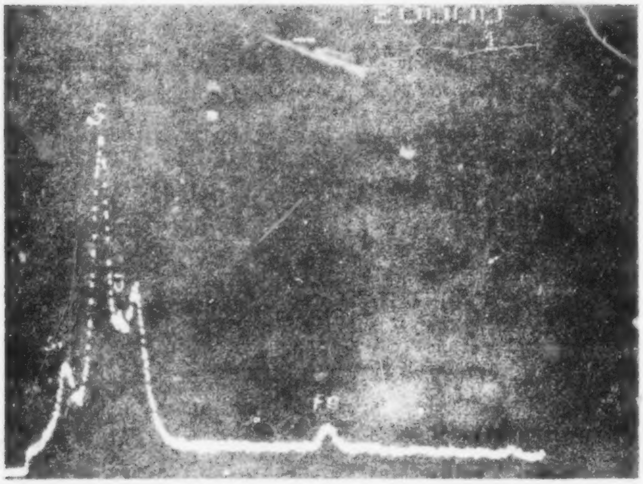
EDX Oscilloscope Trace From Filter 19B

EDX Oscilloscope Trace From Filter 21B

Figure 2-7. Oscilloscope Traces of Si, S and Fe.



EDX Oscilloscope Trace From Filter 27A



EDX Oscilloscope Trace From Filter 30A

Figure 2-8. Additional Oscilloscope Traces of Si, S and Fe.

TABLE 2-8

RESULTS OF X-RAY ANALYSIS

All Five Filters
Type of X-Ray Analysis EDX

Elements Present	Estimated Amount*
S	P
Si	S
Cl	S
Fe	M
Cr	T
Ni	T
Ti	BDT

See accompanying photographs.

*Code

Primary element - P
Secondary - S
Minor - M
Trace - T

This species may be present in foundry effluents.

2.2.3 Conclusions

A number of modifications must be made to the EPA procedure for sampling sulfur oxides from foundries. These include a vycor or quartz probe liner to withstand the high temperatures and a *fine particulate filter must be used* in conjunction with the glass wool plug. One definite advantage is that the barium ion titration procedure gives sharper endpoint determinations. No modifications to the analytical methods are necessary if the fine filter is employed. Only a fraction (∿ 15%) of the sulfur in the coke appears as SO_2. COS may be a product in the effluent of a foundry based on the reaction of excess CO with SO_2.

2.3 KRAFT PULPING

2.3.1 Sources of SO_2 in a Kraft Mill

The kraft pulping process is responsible for the major portion of all pulp manufactured at the present time. The processing which involves hydrolysis of lignin produces odorous compounds such as sulfides, disulfides, mercaptans, etc. Some characteristics of the kraft pulping operation are given in Table 2-9. The recovery of the spent (black) liquor is a very important facet of the kraft process and is the largest potential source of SO_2. The black liquor is concentrated, burned, and limed as indicated in Figure 2-9. Referring to the flow diagram (Figure 2-9), the following table (Table 2-10) from Environmental Engineering (1971a) indicates the approximate range of SO_2 emissions.

From Table 2-10, we see that the *major* source of SO_2 emissions is from the recovery furnace where the black liquor is burned. The logical sampling locations would be before the direct contact evaporator (if possible) and at the outlet of the recovery furnace. Some typical conditions in a recovery boiler flue gas are as follows:

TABLE 2-9

CHARACTERISTICS OF KRAFT PULPING

Cellulosic raw material	Almost any kind of wood, soft or hard
Principal reaction in digester	Hydrolysis of lignins to alcohols and acids; some mercaptans formed
Composition of cooking liquor	12.5% solution of NaOH, Na_2S, and Na_2CO_3. Typical analysis of solids: 58.6% NaOH, 27.1% Na_2S, 14.3% Na_2CO_3. Dissolving action due to NaOH and Na_2S. Na_2CO_3 inactive and represents the equilibrium residue between lime and Na_2CO_3 in the formation of NaOH
Cooking conditions	Time 2-5 hr; temp. 340-350 F; pressure 100-135 psi
Chemical recovery	Most of process is devoted to recovery of cooking chemicals, with incidental recovery of heat through burning organic matter dissolved in liquor from wood; chemical losses from system are replenished with salt cake, Na_2SO_4
Materials of construction	Digesters, pipelines, pumps, and tanks can be made of mild steel or, preferably, of stainless
Pulp characteristics	Brown color; difficult to bleach; strong fibers; resistant to mechanical refining
Typical paper products	Strong brown bag and wrapping; multiwall bags, gumming paper, building paper; strong white papers from bleached kraft; paperboards such as used for cartons, containers, milk bottles, and corrugated board

From R. Shreve, "Chemical Process Industries," McGraw-Hill, New York (1967).

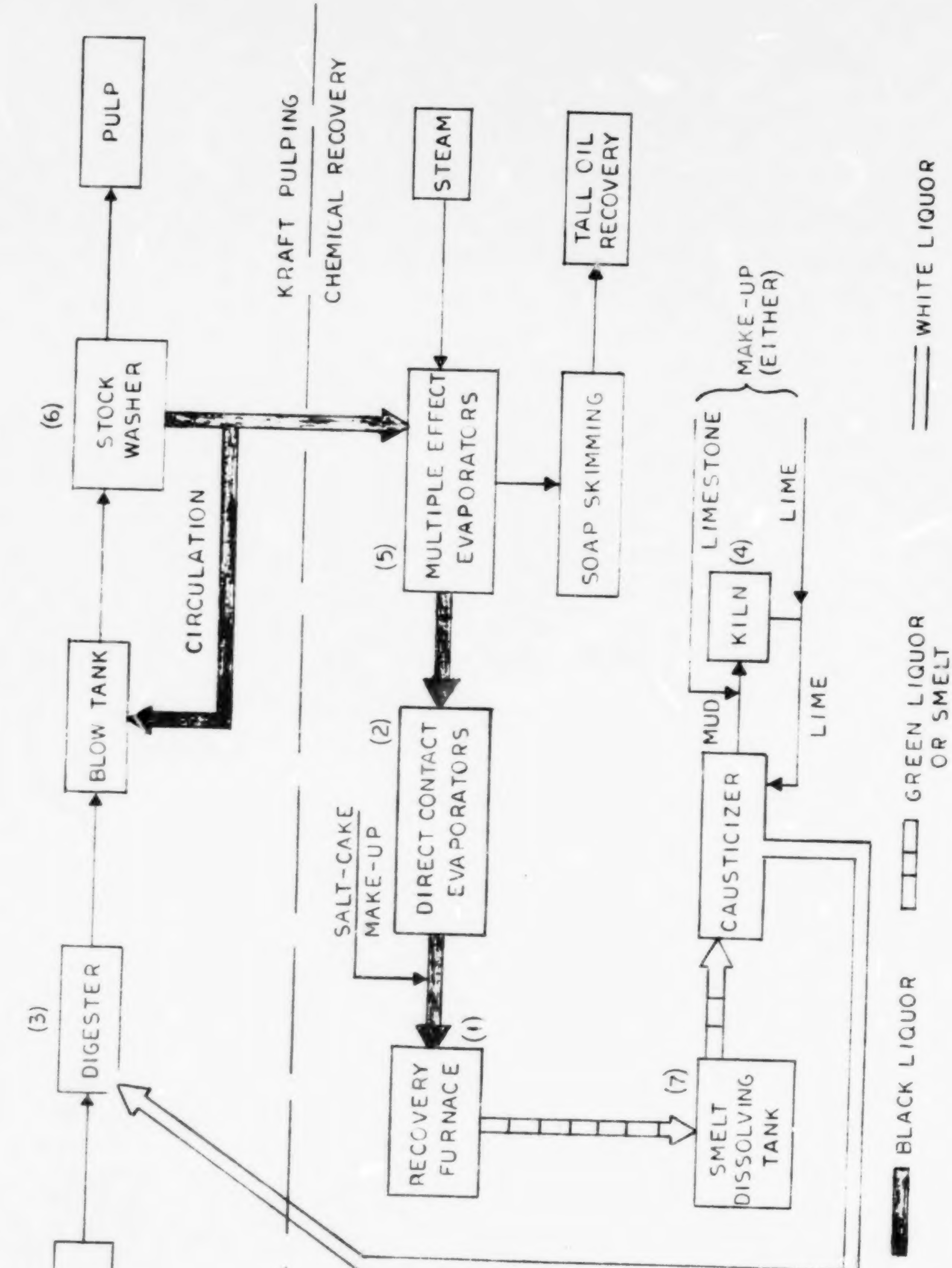

KRAFT PULPING
CHEMICAL RECOVERY
CHIPS
(3)
DIGESTER
BLOW TANK
CIRCULATION
(6)
STOCK WASHER
PULP
SALT-CAKE MAKE-UP
(1)
RECOVERY FURNACE
(2)
DIRECT CONTACT EVAPORATORS
(5)
MULTIPLE EFFECT EVAPORATORS
STEAM
SOAP SKIMMING
TALL OIL RECOVERY
(7)
SMELT DISSOLVING TANK
CAUSTICIZER
MUD
LIME
(4)
KILN
LIMESTONE
LIME
MAKE-UP (EITHER)
BLACK LIQUOR
GREEN LIQUOR OR SMELT
WHITE LIQUOR

FIGURE 2-9 TYPICAL FLOW DIAGRAM FOR KRAFT PULPING

TABLE 2-10

SO_2 EMISSIONS FROM KRAFT PULPING PROCESS

Potential Source		SO_2 Emission lb/ADT*
(1)	Recovery Furnace (before DCE)	0.5-15
(2)	Recovery Furnace (after DCE)	0.5-8
(3)	Digester Relief and Blow	Trace-0.01
(4)	Lime Kiln	Trace
(5)	Multiple Effect Evaporators	0-0.01
	BL Oxidation Tower	0-0.01
(6)	Brown Stock Washers	0.01-0.02
(7)	Smelt Tank	0-0.1

---

*Air dried pulp

Flow to stack: T/D x 300 = acfm

Temp to stack: ∿ 325°F

SO_2 concentration

between boiler & evap	∿ 150 ppm
after evap	∿ 70 ppm

(Note: Dust (Na_2SO_4) load will decrease as one moves from (1) after boiler to (2) after evap to (3) after electrostatic precipitator.)

The SO_2 and total reduced sulfur (TRS) values may vary considerably with time as shown in Figure 2-10. We see that when the operation of a recovery furnace was carried out under optimum conditions, the SO_2 could vary from a few ppm to as high as several hundred ppm. We should point out, however, that the values less than 50 ppm are the most typical of a furnace that is functioning properly.

2.3.2 Sampling and Analytical Results

From the previous section, we have seen that the major SO_2 emissions in a kraft pulping operation can be ascribed to the recovery boiler. Since the particulate matter from the recovery furnace consists of fine particles of Na_2SO_4 and both the barium ion titration and barium chloranilate methods are specific for sulfate, an additional heated (0.3μ) particulate filter was a necessary modification to the conventional EPA SO_2 sampling train (Figure 2-4). The components used for collection of the field samples are listed below:

a. heated glass lined probe with glass wool plug
b. heated (0.30μ) glass fiber filter
c. impingers (2) filled with aqueous H_2O_2
d. metering system (orifice or rotameter plus dry test meter)
e. vacuum pump

The train used is essentially that shown in Figure 2-4b *except that the 80% IPA (SO_3) impingers were eliminated*. A schematic of the kraft mill is shown in Figure 2-11. Two different locations were selected for sampling; one at

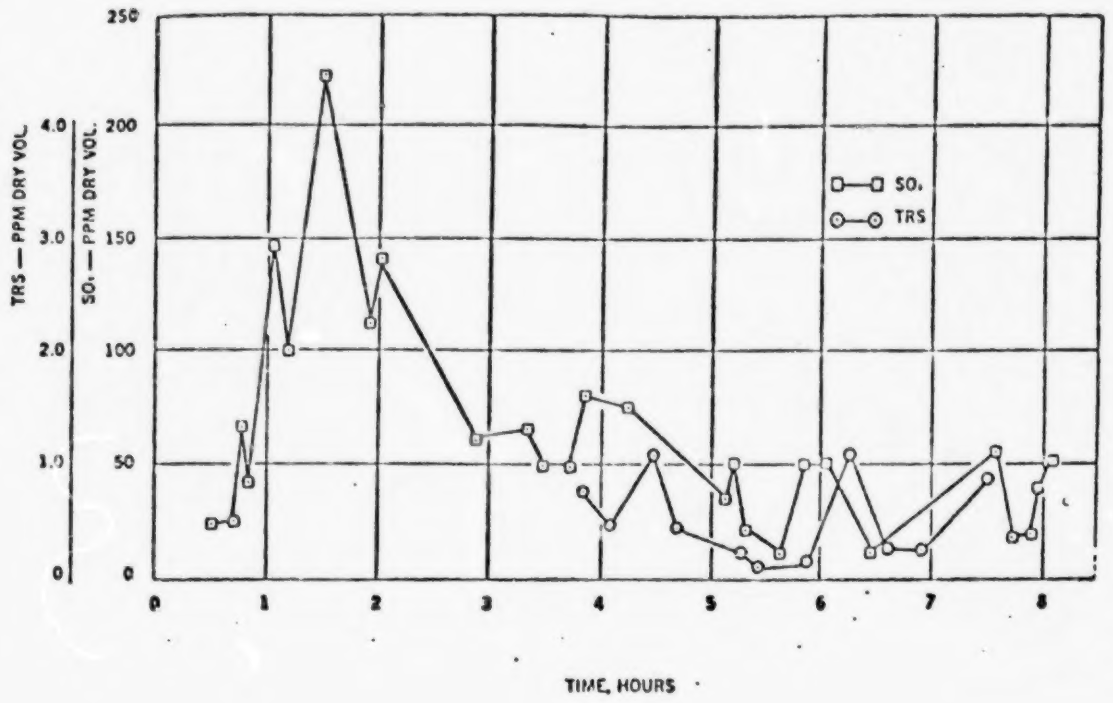
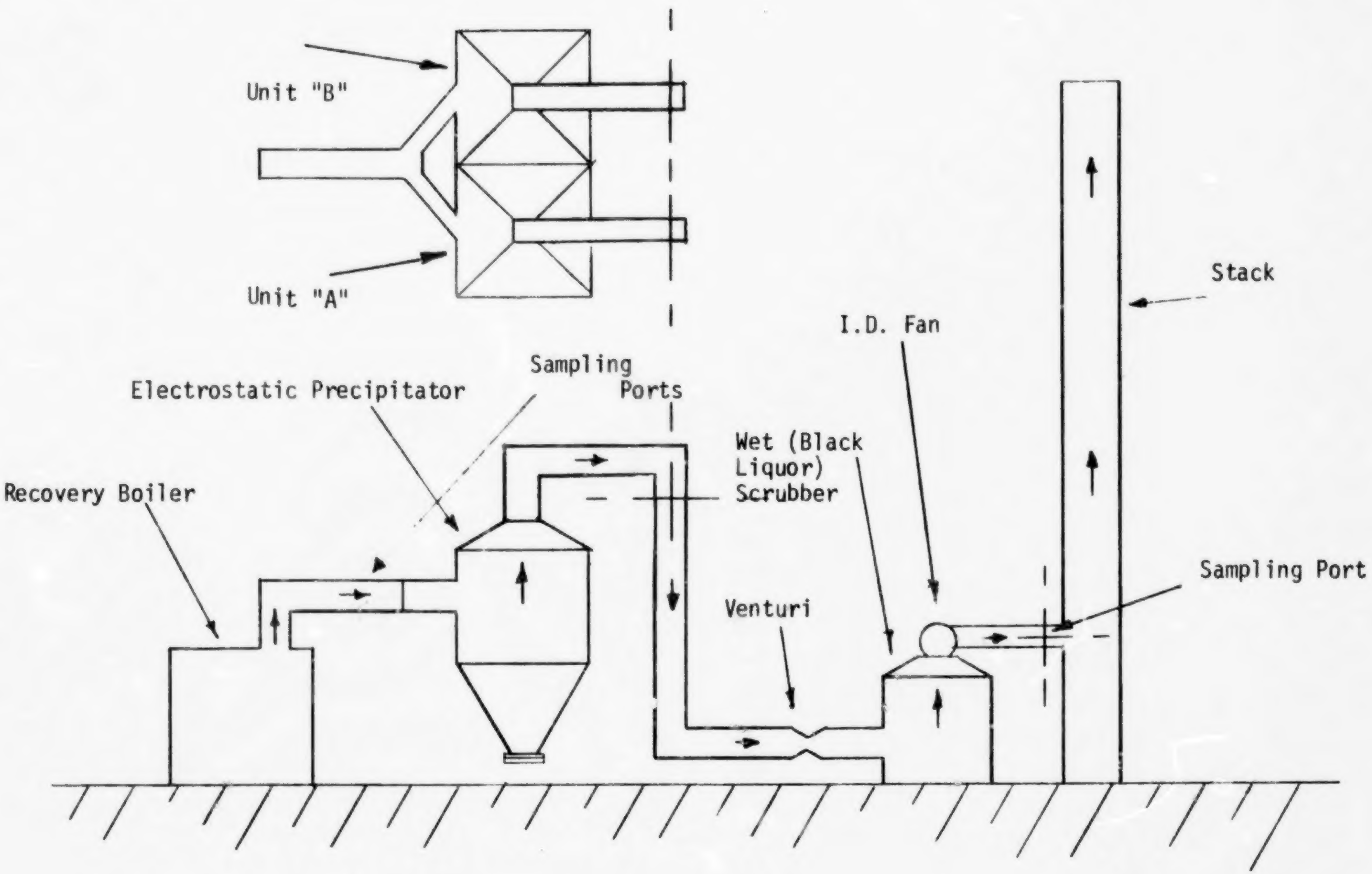


Figure 2-10. Gaseous Sulfur Distribution.

From Environmental Engineering (1971a).



Unit "B"
Unit "A"
Stack
I.D. Fan
Sampling Ports
Electrostatic Precipitator
Wet (Black Liquor) Scrubber
Recovery Boiler
Sampling Port
Venturi

Figure 2-11. Schematic of Kraft Mill Operation.

the inlet of the precipitator; the other at the outlet of the wet scrubber (inlet to the stack). A detailed drawing of the two selected sites is given in Figure 2-12.

For the SO_2 data in Table 2-11 up to run 38, two peroxide absorption trains were run in parallel (A & B represent the two different trains) following the fine particulate filter. The data indicate very low SO_2 levels *both* in the wet scrubber outlet and in the inlet to the precipitator. In runs 19 and 20, the effectiveness of the filter is clearly demonstrated. These high "apparent SO_2" values were due to a leak in the filter which allowed some particulate matter (Na_2SO_4) to be collected in the impingers.

A Barton titrator was run in conjunction with the wet chemical samples up through about run 40. The SO_2 values from the Barton titrator were negligible (< 5 ppm) in all cases. This finding is in agreement with the low values obtained with the barium chloranilate and barium ion titration methods. The volume of stack gas pulled through the peroxide impingers ranged from 60-90 liters over a 30-minute period.

Since the West-Gaeke (1956) method is *specific* for SO_2 and has been used in kraft mill effluents, we compared this sensitive sulfite specific method to those which involve oxidation of the SO_2 to sulfate.

For runs 39-62, three sampling trains were operated in parallel; two contained H_2O_2 absorbing solution and the third was filled with sodium tetrachloromercurate (TCM). The sampling rates were about 3 liters/min and 0.5 liters/min for the peroxide and TCM trains, respectively. The sampling times were 20-30 minutes. The data are given in Table 2-11. Some additional data on temperatures, flue gas composition, etc., are given in Table 2-12.

The results obtained by the three methods* show reasonably good agreement. The sulfate methods, however, suffer from a lack of sensitivity

---

*A fourth method involving potentiometric titration of sulfate with Pb^{++} solution and monitored with a lead ion selective electrode is described in Appendix B.

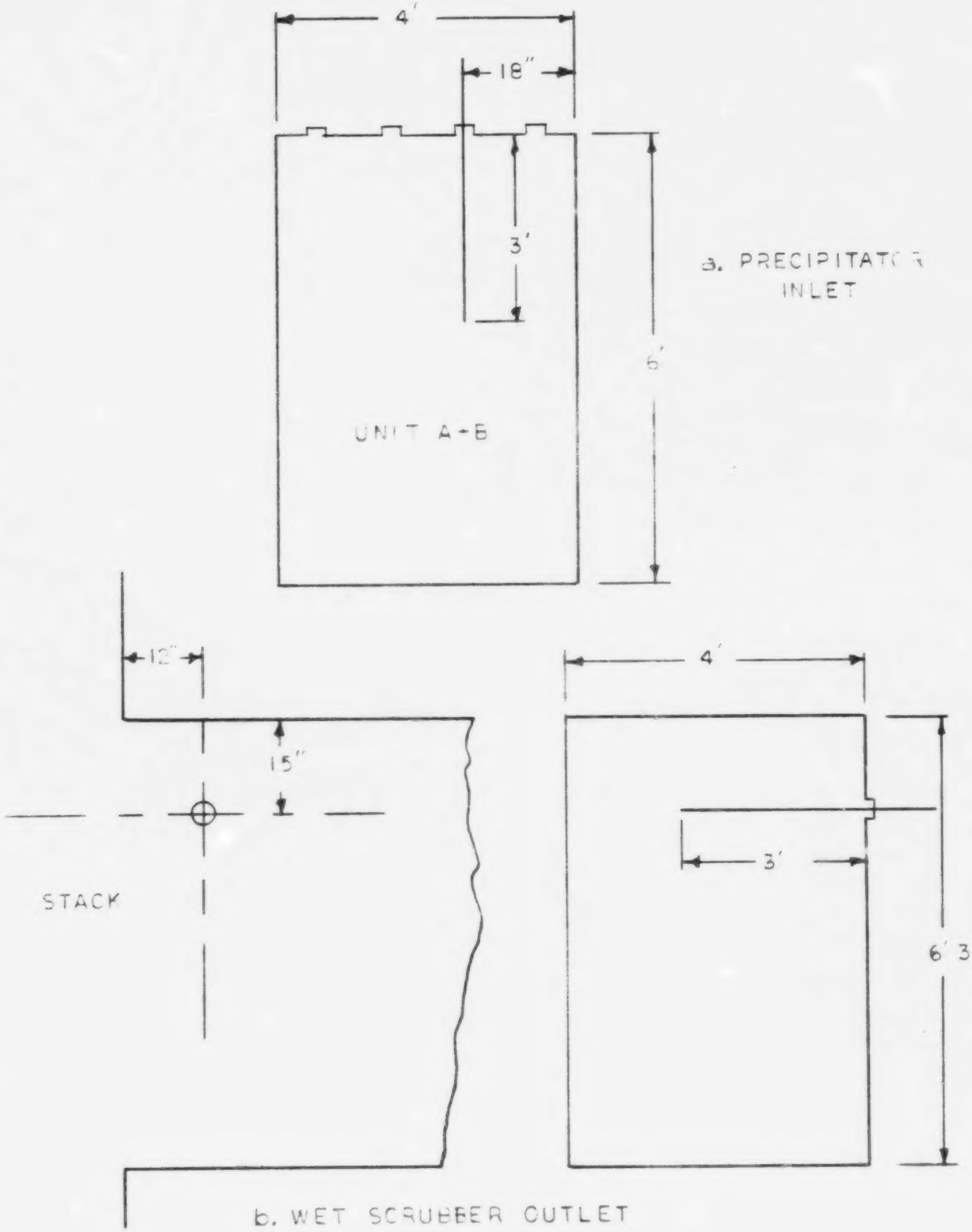

4'
18"
3'
6'
UNIT A+B
a. PRECIPITATOR INLET
12"
15"
STACK
4'
3'
6' 3"
b. WET SCRUBBER OUTLET

Figure 2-12. Detailed Layout of Kraft Mill Sampling Sites.

TABLE 2-11

SO_2 TEST RESULTS FROM A PULP AND PAPER MILL

Sample No.	ppm SO_2 †† (Ba^{++})	ppm SO_2 †† (Ba Chlor)	ppm SO_2 (West-Gaeke)
1A*	4	4	
1B*	18	6	
2A	4	4	
2B	20	16	
3A	5	6	
3B	6	4	
4A	4	2	
4B	10	9	
5A	4	2	
5B	6	8	
6A	3	2	
6B	8	6	
7A	3	2	
7B	0	28	
8A	4	3	
8B	14	4	
9A	6	1	
9B	8	2	
10A	5	1	
10B	8	4	
11A	4	4	
11B	9	10	
12A	4	5	
12B	8	7	
13A	4	4	
14A	4	0	
15A	3	0	
16A	3	2	
17A	2	4	
18A	3	4	
19A	174	198 } filter	
20A	192	221 } leaking	
21A	4	0	
21B	2	0	
22A	6	4	
22B	4		
23A	5	0	
23B	4		
25A	1	4	
25B	1	1	
26A	2	4	
26B	2	3	
27A	2	3	
27B	2	4	

TABLE 2-11 (continued)

Sample No.	ppm SO_2 ++ (Ba^{++})	ppm SO_2 ++ (Ba Chlor)	ppm SO_2 (West-Gaeke)
28A	1	4	
28B	1	2	
29A	1	4	
29B	1	2	
30A	0	2	
30B	0	0	
31A	1	1	
31B	1	0	
32A	1	2	
32B	1	4	
33A	1	2	
33B	0	2	
34A	1	6	
34B	2	10	
35A	0	1	
35B	0	2	
36A	0	2	
36B	0	4	
37A	1	2	
37B	0	3	
38A	0	1	
38B	0	2	
39A	3	5	
39B	2	4	1.8
40A	2	2	
40B	2	6	1.8
41A	1	2	
41B	2	6	1.2
42A	2	2	
42B	2	2	1.2
43A	1	5	
43B	1	2	1.2
44A	1	2	
44B	2	2	0.4
45A	1	2	
45B	1	0	0.7
46A	1	2	
46B	1	0	0.6
47A	0	0	
47B	0	1	0.7
48A	0	2	
48B	1	2	0.7
49A	0	2	
49B	0	2	0.5
50A	1	1	
50B	0	2	0.5

TABLE 2-11 (continued)

Sample No.	ppm SO_2 [††] (Ba^{++})	ppm SO_2 [††] (Ba Chlor)	ppm SO_2 (West-Gaeke)
51A	0	4	0.5
51B	0	5	
52A	0	2	0.4
52B	0	2	
53A	0	2	0.4
53B	0	2	
54A	0	2	0.5
54B	0	1	
55A	5	2	0.5
55B	6	1	
56A	0	0	0.4
56B	0	2	
58A	14	8	6.6
58B	19	11	
59A	24	21	25.5
59B	38	34	
60A	0	2	0.4
60B	0	0	
61A	4	2	0.4
61B	5	2	
62A	4	2	0.3

[††] These analytical methods (Ba^{++} and Ba Chlor) were run on aliquots of the same sample.

[*] A and B represent results from two parallel trains run off the same probe.

TABLE 2-12

SUPPLEMENTARY DATA FROM THE PULP AND PAPER MILL

Run No.	Date	Sampling Location	% CO_2	% O_2	Stack Temperature (°F)
1-5	12/16/71	Recovery Boiler-Scrubber Outlet	13.5	9	210
6-12	12/17/71	Recovery Boiler-Scrubber Outlet	12.5	8	205
13-18	12/20/71	Recovery Boiler-Scrubber Outlet	12.5	8.5	204
19-21	12/21/71	Recovery Boiler-Precipitator Inlet	12	7	570
22-23	12/22/71	Recovery Boiler-Precipitator Inlet	--	-	620
25-33	12/30/71	Recovery Boiler-Precipitator Inlet	13.5	7.5	565
34-38	12/31/72	Recovery Boiler-Precipitator Inlet	12	7	625
39-40	1/4/72	Recovery Boiler-Precipitator Inlet	13	7	649
41-50	1/5/72	Recovery Boiler-Precipitator Inlet	13	7.5	625
51-59	1/6/72	Recovery Boiler-Precipitator Inlet	12	6	615
60-62	1/7/72	Recovery Boiler-Precipitator Inlet	12	6	540

at these low SO_2 (about 2 ppm) levels* even with the 60-90 liter sample volumes. The West Gaeke method, on the other hand, has adequate sensitivity in this range and may be more useful for determining low SO_2 concentrations, e.g., 1 or 2 ppm.

Statistical analysis of all the data in Table 2-11 (except runs 19 and 20) yields the following results:

$$\text{ppm } SO_2 \text{ (Ba Chlor)} = 1.56 + 0.62 \text{ ppm } SO_2 \text{ (Ba}^{++}\text{)}$$

Correlation Coefficient = 0.71

$$\text{ppm } SO_2 \text{ (West Gaeke)} = -\ 0.18 + 0.72 \text{ ppm } SO_2 \text{ (Ba}^{++}\text{)}$$

Correlation Coefficient = 0.95

$$\text{ppm } SO_2 \text{ (West Gaeke)} = -\ 1.3 + 0.93 \text{ ppm } SO_2 \text{ (Ba Chlor)}$$

Correlation Coefficient = 0.98

The three methods agree well with each other over this rather limited and low range of SO_2 concentrations.

2.3.3 Conclusions

The SO_2 concentrations found in a recovery furnace of a kraft mill were very low. The average SO_2 concentration was less than 10 ppm with samples collected randomly over a three week period. The sulfate specific methods require a fine particulate filter to remove Na_2SO_4 particles in the recovery boiler stack. The two *sulfate* specific methods (barium ion titration and barium chloranilate colorimetric) yield results for SO_2 which are in excellent agreement with the *sulfite* specific method (West Gaeke) in the recovery boiler flue gas.

---

*The sensitivity of the barium chloranilate method can be increased by reading the absorbance at 330 nm instead of 530 nm.

2.4 IRON AND STEEL

2.4.1 Brief Description of the Iron and Steel Industry

The major pollutant emitted from the iron and steel industry is particulate matter. Emissions of sulfur oxides are derived from the sulfur in the fuel and other raw material processes.

A detailed breakdown of the emission of SO_2 to the atmosphere for 1967 from Varga, et al. (1969) is given in Table 2-13 for the iron and steel industry. With the exception of fossil fuels (oil and coal) used in various processes, the production of coke from coal and the use of the by-product coke in various metalmaking processes accounts for the major portion of SO_2 emissions. Clearly, these potential sources dictate the necessary sites selected for SO_2 sampling.

Iron and steel processing can be divided into three closely allied but separate operations:

a. coking
b. sintering
c. metalmaking process

2.4.1.1 Coking

In the coke ovens, finely ground (1/8 inch) coal is burned in an enclosure with a reducing atmosphere (inadequate oxygen for complete combustion). The resulting product consists primarily of carbon with a small amount of sulfur (∿ 0.6%). The off-gases from coking consist of carbon monoxide, hydrogen, methane, hydrogen sulfide, sulfur dioxide, ammonia, nitrogen, and many high molecular weight organic compounds. A typical composition of the major constituents of coke oven gas is shown in Table 2-14.

The commonly used "slot type" coke oven is a narrow refractory channel which may be up to 60 feet long, 18 feet high and 20 inches wide. These ovens are grouped in "batteries." The flues between the adjoining ovens are heated to produce the high temperatures necessary to drive the volatile matter from the coal to produce coke.

TABLE 2-13

EMISSIONS OF SULFUR OXIDES TO THE ATMOSPHERE FROM THE IRON AND STEEL INDUSTRY (1967)

	Tons SO_2/year Emitted to the Atmosphere	% of Total
Coke Oven Gas	392,000	52
Coke Breeze	48,000	6.4
Fuel Oil	154,000	21
Coal	138,000	18.4
Tar and Pitch	16,000	2.2

From Varga, et al. (1969).

TABLE 2-14

COMPOSITION OF COKE OVEN GAS

Component	Volume %
CO_2	1.8
O_2	0.2
N_2	3.4
CO	6.3
H_2	53.0
CH_4	31.6
C_2H_4	2.7
C_6H_6	1.0

Density = 0.03 #/ft^3

From "Combustion Calculations by Graphical Methods," Combustion Engineering (1970).

The ovens are loaded from the top through several charging ports which are covered and sealed for the coking operation. The gases generated during coking are collected by a ducting system at the top of the "slot" oven and sent to a by-product recovery operation. About 40% of these gases are cleaned and burned to generate heat for the operation of the coke ovens.

The exhaust from the heating units is usually vented through a single stack. The combustion of the cleaned coke oven gas generates some sulfur dioxide since the original gas may have contained as much as 3 to 5 grains of sulfur (as H_2S) per cubic foot.

At the conclusion of the coking cycle, the end doors are removed and a mechanical ram pushes the coke out of the oven into a special car which carries the coke to a quenching operation.

2.4.1.2 Sintering

In order to process iron ore in a blast furnace, it is necessary for the particle size to be increased to prevent losses out the top of the furnace.

In the sintering process, iron ore, furnace flue dust, miscellaneous fines, and other iron-bearing materials are mixed with limestone and *coke breeze* or *coal* and fed to a sinter machine where it is combusted on a steel conveyor.

The material is ignited and the combustion is self-supporting. Combustion air is drawn through a sinter bed which has the underlying sections separated into individual compartments to ensure uniform air distribution. These compartments, called "wind boxes", are ducted to a single fan. The ore thus heated is collected in cyclones and electrostatic precipitators and then sent to the blast furnace.

The sintering operation is not as large a source of sulfur oxide emissions as the coke ovens but the quantity of sulfur in the raw materials and the fuel is still considerable. It has been estimated that approximately two pounds of sulfur are introduced in the sintering process during the production of one ton of sinter. Approximately one-half of the sulfur is in the iron ore and the other half is in the coke, fuel and limestone (Varga, 1969).

A liquid slag which is formed in the sintering process retains approximately 64% of the sulfur with the remainder (36%) leaving the system in the combustion gases. This is equivalent to several hundred ppm of SO_2 in the stack gases (Environmental Engineering, 1971b).

2.4.1.3 Metalmaking Process

The open hearth furnaces which were once the primary units in the iron and steel-making industry are being phased out and the Basic Oxygen Furnaces (BOF) are taking their place. With the open hearth, about 50% of the sulfur input goes into the steel and slag and about 50% goes out as SO_2 in the flue gas (Varga, 1969). The SO_2 level in the flue gas could be as high as 250 ppm if all the sulfur in the process feed were converted to SO_2.

2.4.1.4 Summary

1. The principal source of sulfur emissions in the iron and steel processes is in the coal used for the production of coke, and the coke used in the sintering and metalmaking processes.

2. The sources to be sampled should include the coking process as well as the operations using large quantities of coke, e.g., open hearth and sintering.

2.4.2 Sampling and Analytical Results

The following operations were tested in an iron and steel plant:

sintering
coke oven
open hearth

Since the flue gas temperatures of these sources were 500°F or less (Table 2-15) the EPA heated probe with a pyrex liner and glass wool filter was used. Three trains (A, B, and C) were run in parallel off the same probe on the coke oven (runs 1-16). In the other sources tested, two and sometimes three trains were run in parallel off the same probe. The sampling trains consisted of two impingers containing 15 ml of 80% isopropanol-20% water followed by two impingers containing 15 ml of 3% aqueous hydrogen peroxide with appropriate metering and air moving devices. During each test, one or two samples were collected behind a *heated* fine (0.3μ) glass fiber particulate filter. The sample volume collected ranged from about 80-100 liters over a thirty minute period. Detailed layouts of the three operations and also the sampling sites are shown in Figures 2-13 to 2-15.

The results for the coke oven, sintering and open hearth test sites are given in Tables 2-16 to 2-19. On the open hearth, a number of runs were eliminated (Table 2-19) because one of the two probes used had a broken liner. Although this probe was checked (leak tested) before it was put into the open hearth stack, the leak was not detected, and no SO_2 was found in these samples. These samples were, for the most part, those which had the fine particulate filter in line.

Statistical analysis of the results from Tables 2-16 to 2-19 are shown in Table 2-20. For the No. 1 coke oven there appears to be no significant difference between the filtered and unfiltered samples for Ba^{++} or Ba Chlor. A semi-quantitative emission spectrographic analysis of an SO_2 impinger sample from a coke oven is shown in Table 2-21. No zinc was found and Cu^{++}, Ca^{++} and other interferences, if present, are at very low concentrations in both the filtered and unfiltered samples. Atomic absorption analysis indicated no detectable quantities of Zn, Ca, or Na in the samples.

The regression equations and correlation coefficients are excellent in both cases. The CV for the Ba^{++} titration at the No. 1 coke oven (1.4%) is very similar to that obtained for the coal-fired power plant (CV = 1.5%) although the mean SO_2 value is slightly lower. The Ba Chlor shows slightly higher CV's than that found for the uncontrolled coal-fired power plant.

TABLE 2-15

SUPPLEMENTARY DATA FROM THE IRON AND STEEL PLANT

Run No.	Date	Sampling Location	% CO_2	% O_2	Stack Temperature (°F)
1-10	2/23/72	Coke oven	4.2	10.5	300
11-16	2/24/72	Coke oven			335
17-25	2/25/72	Coke oven (10% oven gas and 90% blast furnace gas)	16.0	0	160
29-34	2/28/72	Sinterer			313
35-48	2/29/72	Sinterer	0.5	19.0	
49-58	3/1/72	Open hearth	3.5	15.5	480
59-70	3/2/72	Open hearth	2.5	18.0	500

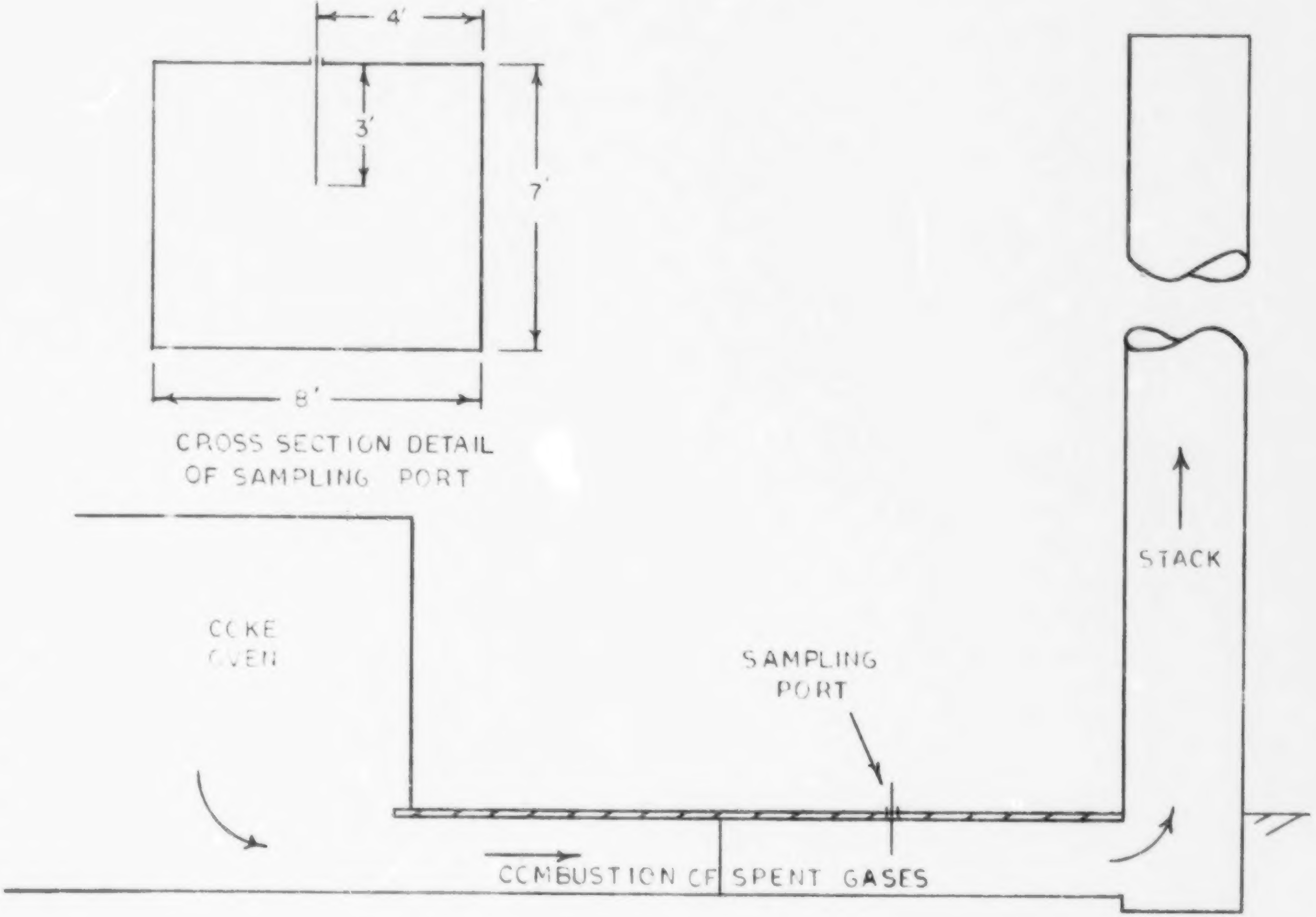

4'
3'
7'
8'
CROSS SECTION DETAIL
OF SAMPLING PORT
STACK
COKE
OVEN
SAMPLING
PORT
COMBUSTION OF SPENT GASES

Figure 2-13. Schematic of Coke Oven Site and Sampling Port.

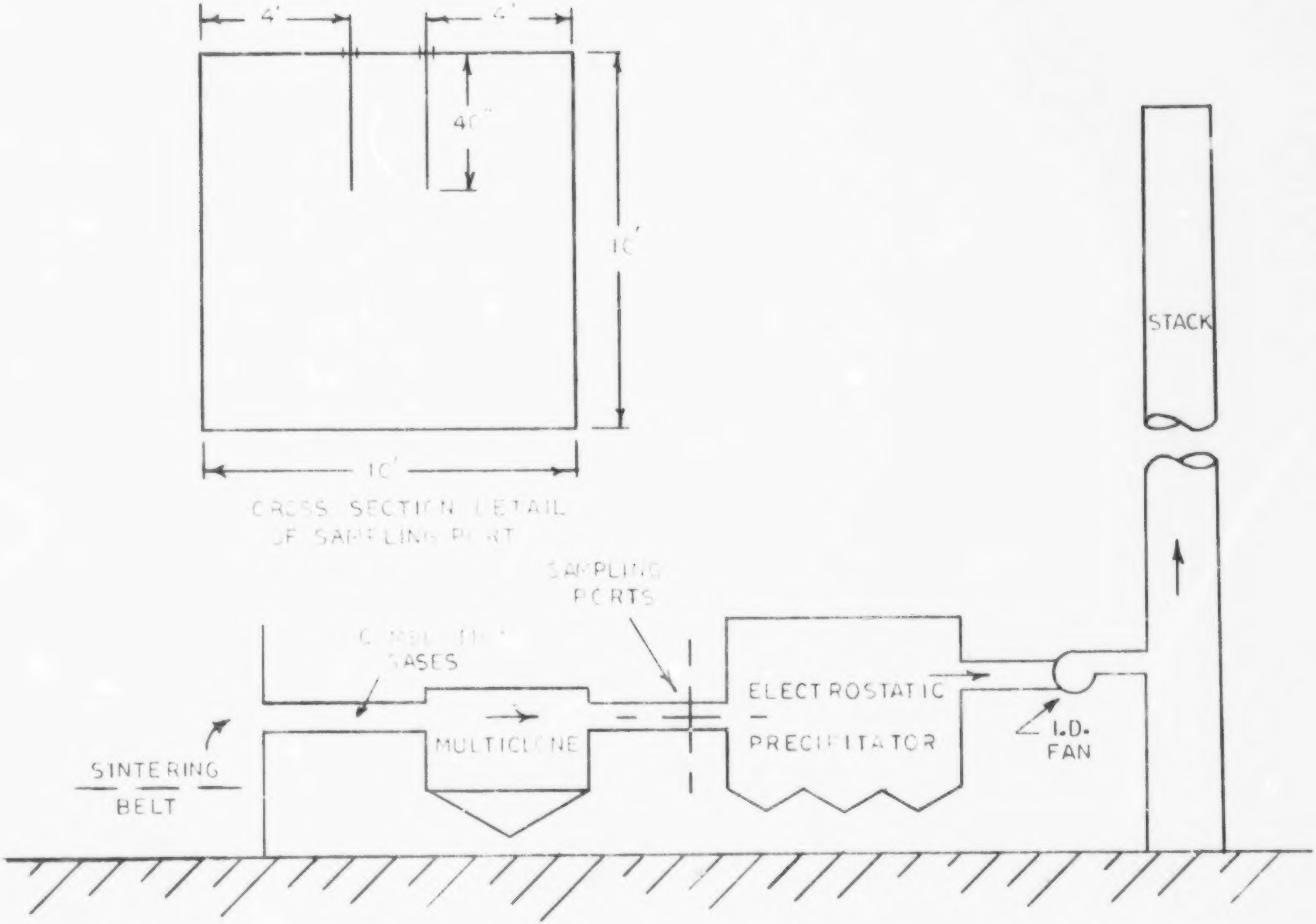

4'
4'
40"
10'
10'
CROSS SECTION DETAIL OF SAMPLING PORT
STACK
SAMPLING PORTS
COMBUSTION GASES
ELECTROSTATIC PRECIPITATOR
I.D. FAN
SINTERING BELT
MULTICLONE

Figure 2-14. Sintering Plant Schematic and Test Site.

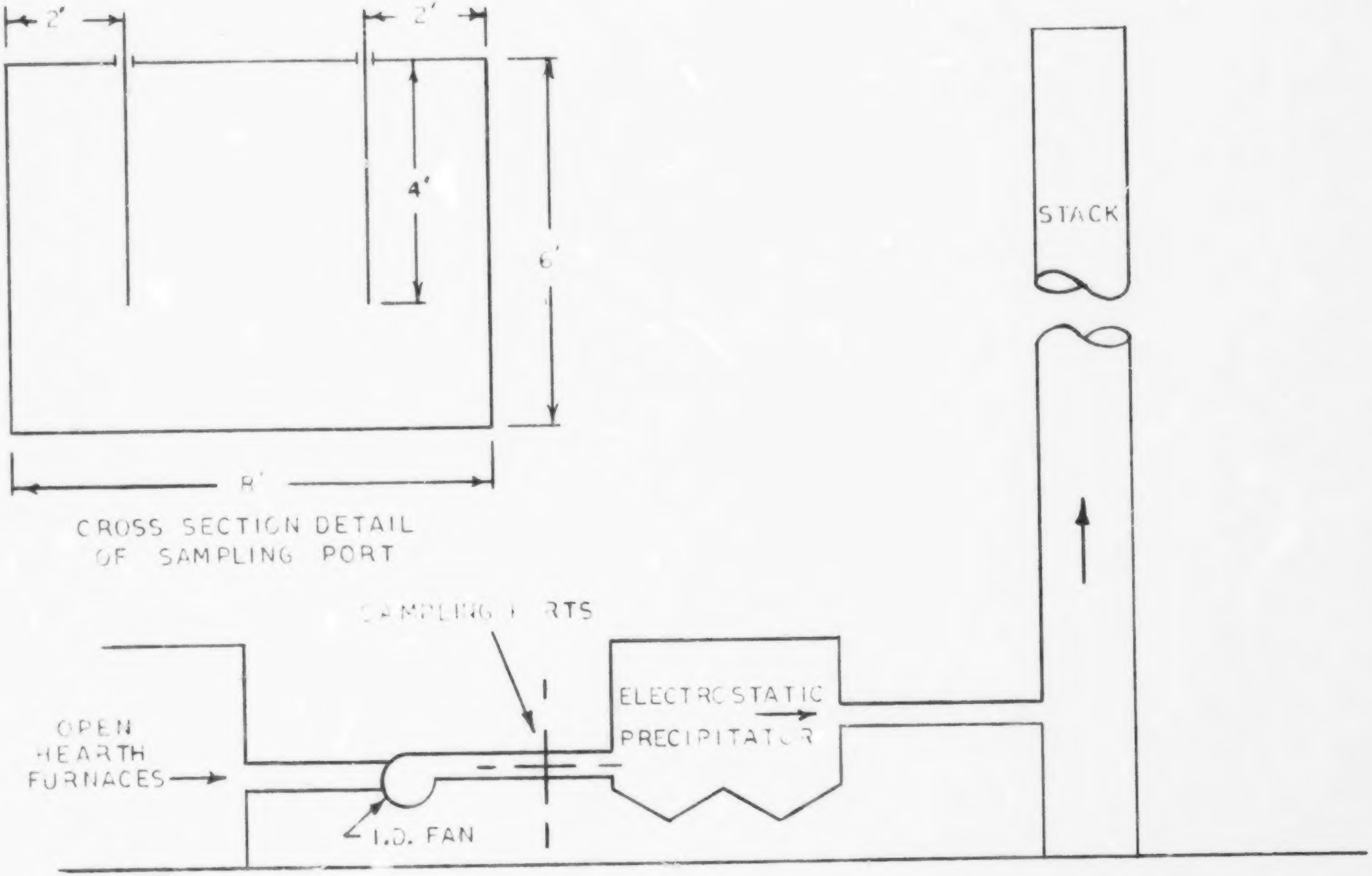

2'
2'
4'
6'
8'
CROSS SECTION DETAIL
OF SAMPLING PORT
STACK
SAMPLING PORTS
ELECTROSTATIC
PRECIPITATOR
OPEN
HEARTH
FURNACES
I.D. FAN

Figure 2-15. Schematic of Open Hearth Unit and Sampling Ports.

TABLE 2-16

SO_2 TEST RESULTS FROM AN IRON AND STEEL PLANT (COKE OVEN)

Sample No.	ppm SO_2 (Ba Chlor)	ppm SO_2 (Ba^{++})	ppm SO_2 (NaOH)
1A †	251	280	300
1B* †	214	258	272
1C †	249	282	302
2A	293	280	302
2B*	158	158	163
2C	281	267	269
3A	273	267	286
3B*	261	267	275
3C	307	295	315
4A	288	282	297
4B*	282	268	285
4C	319	310	330
5A	287	282	301
5B*	257	250	273
5C	281	278	304
6A	135	137	141
6B*	245	238	254
6C	313	310	321
7A	225	230	247
7B*	221	223	239
7C	300	306	327
8A	295	294	301
8B*	301	291	316
8C	334	330	358
9A	287	284	302
9B*	285	282	303
9C	315	315	339
10A	273	273	291
10B*	279	279	292
10C	317	316	327
11A	172	170	182
11B*	135	136	148
11C*	192	188	202
12A	177	177	189
12B*	135	140	147
12C*	165	176	180
13A	162	155	163
13B*	99	116	117
13C*	115	118	118
14A	153	148	
14B*	3	16	
14C*	6	3	

TABLE 2-16 (continued)

Sample No.	ppm SO_2 (Ba Chlor)	ppm SO_2 (Ba++)	ppm SO_2 (NaOH)
15A	214	208	
16A	177	183	

---

*With fine particulate filter

A, B, and C represent results from three parallel trains run from the same probe.

TABLE 2-17

SO_2 TEST RESULTS FROM AN IRON AND STEEL PLANT (COKE OVEN)†

Sample No.	ppm SO_2 (Ba Chlor)	ppm SO_2 (Ba^{++})
17A*	51	59
17B*	53	64
18A*††	29	43
18B*††	33	41
18C ††	35	44
19A	38	46
19B	39	42
20A*	23	28
20B*	21	29
21A	29	34
21B	29	34
22A*	32	36
22B*	32	33
23A	28	31
23B	34	30
24A*	36	37
24B*	35	36
25A	26	32
25B	28	28

---

[*] With fine particulate filter

[†] 90% blast furnace gas, 10% coke oven gas

[††] A, B, and C represent results from three parallel trains run from the same probe

TABLE 2-18

SO_2 TEST RESULTS FROM AN IRON AND STEEL PLANT (SINTERER)

Sample No.	ppm SO_2 (Ba Chlor)	ppm SO_2 (Ba++)
29A †	25	20
29B* †	30	24
29C* †	38	28
30A	22	14
30B*	22	20
30C	20	21
31A	18	20
31B*	26	20
31C*	18	18
32A	10	16
32B*	8	12
32C*	6	9
33A	8	12
33B*	14	12
33C*	16	16
34A	13	15
34B*	18	19
34C*	21	22
35A	24	23
35B	23	28
36A*	4	0
36B*	10	10
37A	5	0
37B	34	34
38A*	13	14
38B*	16	18
39A	46	45
39B	44	44
40A*	24	24
40B*	26	26
41A*	28	25
41B*	34	29
42A	49	50
42B	52	52
43A*	25	28
43B*	28	30
44A	16	0
44B	14	14
45A*	22	25
45B*	22	25
46A	40	44
46B	47	48

TABLE 2-18 (continued)

Sample No.	ppm SO_2 (Ba Chlor)	ppm SO_2 (Ba++)
47A*	25	28
47B*	24	26
48A	51	51
48B	42	43

---

[*] With fine particulate filter

[†] A, B, and C represent results from three parallel trains run from the same probe.

TABLE 2-19

SO_2 TEST RESULTS FROM AN IRON AND STEEL PLANT (OPEN HEARTH)

Sample No.	ppm SO_2 (Ba Chlor)	ppm SO_2 (Ba^{++})
49A †	34	36
49B* †	12	14
49C* †	54	56
50A	28	34
50B*	111	106
51A	66	64
51B*	62	58
51C*	70	66
53A	43	44
53B	44	44
55A	36	38
55B	32	36
57A	38	42
57B	42	46
60A	38	39
60B	34	40
62A	8	20
62B	12	20
63A	46	48
63B	48	51
65A	35	42
65B	38	40
67A	50	52
67B	56	55
69A	27	30
69B	32	35

---

*With fine particulate filter

†A, B, and C represent results from three parallel trains run from the same probe.

TABLE 2-20

STATISTICAL ANALYSIS FOR SO_2 TEST RESULTS FROM AN IRON AND STEEL PLANT

Site	Run No.	Regression Equation	Correlation Coefficient	Coefficient of Variation of Analytic Method	Mean
#1 Coke Oven	1-16*	ppm Ba^{++} = 0.97 ppm Ba Chlor + 5.6	0.98		
	1-16*			(Ba Chlor) 5.9%	257
	1-16*			(Ba^{++}) 1.2	256
	1-16†	ppm Ba^{++} = 0.99 ppm Ba Chlor + 2.8	0.99		
	1-16†			(Ba Chlor) 4.9%	257
	1-16†			(Ba^{++}) 1.6	212
#8 Coke Oven	17-25*	ppm Ba^{++} = 1.17 ppm Ba Chlor - 4.5	0.89		
	17-25*			(Ba Chlor) 9.7%	38
	17-25*			(Ba^{++}) 3.6	35
	17-25†	ppm Ba^{++} = 1.00 ppm Ba Chlor + 3.4	0.95		
	17-25†			(Ba Chlor) 7.2%	33
	17-25†			(Ba^{++}) 4.2	40
Sinterer	29-48*	ppm Ba^{++} = 1.06 ppm Ba Chlor - 3.2	0.97		
	29-48*			(Ba Chlor) 12.3	21
	29-48*			(Ba^{++}) 2.9	28
	29-48†	ppm Ba^{++} = 0.81 ppm Ba Chlor + 3.6	0.91		
	29-48†			(Ba Chlor) 7.2	29
	29-48†			(Ba^{++}) 4.7	20
Open Hearth	49-70*	ppm Ba^{++} = 0.93 ppm Ba Chlor + 5.4	0.99		
	49-70*			(Ba Chlor) 8.8	37
	49-70*			(Ba^{++}) 5.0	35

---

* Just glass wool filter

† With fine particulate filter and glass wool filter

TABLE 2-21

SEMIQUANTITATIVE SPECTROGRAPHIC ANALYSIS OF AN SO_2 IMPINGER SAMPLE FROM AN IRON AND STEEL PLANT (COKE OVEN)

	ppm Al	ppm B	ppm Be	ppm Cu	ppm Cr	ppm Fe	ppm Mg	ppm Mn	ppm Ni
With glass wool filter	0.05-0.5	--	--	0.1-1	0.03-0.3	0.1-1	0.03-0.3	0.003-0.03	0.01-0.1
With glass wool and fine particulate filter	0.03-0.3	--	--	0.1-1	0.003-0.03	0.03-0.3	0.03-0.3	0.001-0.01	0.003-0.03

	ppm Ag	ppm Pb	ppm Sn	ppm Ca	ppm Si	ppm Ti	ppm Zn	ppm Na
With glass wool filter	0.03-0.3	0.03-0.3	--	0.03-0.3	0.03-0.3	0.003-0.03	--	0.1-1
With glass wool and fine particulate filter	0.1-1	0.03-0.3	--	0.03-0.3	0.03-0.3	0.003-0.03	--	0.3-3

The No. 8 coke oven effluent which is ~ 10% coke oven gas and 90% blast furnace gas does show a slight improvement with the fine particulate filter but this is not significant because of the low concentrations of SO_2 in the flue gas which produces added variability in the methods. The small difference in CV values for filtered versus unfiltered samples indicate no interference for Ba^{++} or the barium chloranilate methods (the increased CV is due to the lower SO_2 level).

The sintering operation also has low SO_2 concentrations and the difference between filtered and unfiltered samples is negligible. The chloranilate method, however, does show an apparent improvement in the CV vor the filtered. However, the regression equation is somewhat poorer.

The Ba^{++} and Ba Chlor methods agree well for the unfiltered (without fine particulate filter) samples. The filtered samples (with a few exceptions) were run on the other probe which had a cracked probe liner. The CV for Ba^{++} is probably typical for these low SO_2 levels. It is not clear whether the higher CV for Ba Chlor is due to an interference or the imprecision of the method at this SO_2 level.

The sulfur balance[*] for a coke oven operation is given in Table 2-22. The calculated SO_2 value (ppm by volume) *if all of the sulfur* in the coke oven gas *was oxidized* would be about 1000 ppm. The average measured value for samples 1-10 (by Ba^{++}) is 295 ppm. The measured O_2 value in Table 2-15 indicates a dilution of the flue gas with approximately one volume of air. On this basis, the measured values should be adjusted to give about 600 ppm SO_2. This is 60% of the calculated value. We have been in Table 2-14 that the flue gas from a coke oven is a reducing atmosphere with several percent carbon monoxide. For a blast furnace, which also has a reducing atmosphere, the Bureau of Mines (1968) has reported that no sulfur oxides are present in the top gases. We have seen previously that in the foundry which is operated in a reducing atmosphere to prevent oxidation of

---

[*] An actual sulfur balance carried out on the coke ovens which we sampled was in good agreement with that in Table 2-22.

TABLE 2-22

SULFUR BALANCE FOR COKE OVEN OPERATION
(Based on Production of One Net Ton of Coke)

Item	Amount, pounds	Sulfur, percent	Amount of Sulfur, pounds
	Input		
Coal	2950	0.8	23.60
	Output		
Coke and breeze	2121	0.700	14.85
By-products	290	0.344	1.00
Coke-oven gas[a]	534	1.45	7.75
		Total	23.60

(a) Coke-oven gas produced is 15,000 ft^3.

the metal in the melt, approximately 50% of the sulfur in the flue gas is emitted as SO_x and a large portion remains as sulfur in the particulate matter or dissolved in the melt. Thus, the approximately 60% of theoretical SO_2 obtained here is not unreasonable. The CO may react with SO_2 to form elemental S (Ryason and Harkins, 1967). The data on runs 17-25 were obtained in a coke oven which consists of 90% blast furnace gas and 10% coke oven gas. Since the blast furnace contains no SO_2, the values would be expected and are found to be about 10% of the concentration of runs 1-16.

The sulfur balance for the sintering operation is shown in Table 2-23. From the estimated sulfur in the combustion gases and the quantity of fuel, the SO_2 concentration is calculated to be approximately 250 ppm. The average measured SO_2 values obtained from the sintering operation (Ba^{++} runs 29-48) is 20 ppm. The CO_2 and O_2 data in Table 2-15 indicates dilution of the flue gas with about 15 volumes of air. If we now correct the measured value for this dilution, we obtain about 300 ppm SO_2. This difference between measured and calculated SO_2 may be the result of a different sulfur content in the fuel oil and/or the large dilution factor determined by O_2 and CO_2 measurements. However, in view of the many approximations made, the agreement is reasonable, e.g., all of the sulfur is emitted as SO_2.

The sulfur balance for an open hearth furnace from Varga (1969) indicates that nearly 50% of the sulfur goes into the slag or steel and the remainder is emitted to the atmosphere. The calculated value for SO_2 then is of the order of 200 ppm. The measured (average) SO_2 value from the open hearth is 45 ppm or 180 ppm when corrected for the approximately four-fold dilution of the flue gas with air (determined by O_2 and CO_2 measurements in Table 2-15). This value is quite reasonable since it represents approximately 90% of the predicted SO_2 level in the open hearth. No fuel, slag or scrap samples were taken for sulfur analysis.

For the latter two sites, all the sulfur would be converted to SO_2 since these conditions are similar to a combustion environment.

TABLE 2-23

SULFUR BALANCE FOR SINTERING MACHINE OPERATION
(Based on the Production of One Net Ton of Sinter)

Item	Amount, pounds	Sulfur Content, percent		Amount of Sulfur, pounds
		Input		
Iron-bearing material	2200	0.041		0.90
Coke	100	0.70		0.70
Oil	50	0.55		0.27
Limestone	200	0.049		0.10
			Total	1.97
		Output		
Sinter	2000	0.055		1.10
Sinter fines	289	0.055		0.16
SO_2 in exhaust gases				0.71
			Total	1.97

2.4.3 Conclusions

No major interferences with the analytical methods appear to be present in the sources sampled in the iron and steel industry. The sharper endpoint for Ba^{++} titrations obtained with the fine particulate filter in the sampling train suggest that this be used, however. The limited data suggest that part of the sulfur from the coke ovens is retained in the particulate because of the reducing atmosphere, while in the open hearth and sintering operations, the estimated and measured SO_2 values show reasonable agreement.

2.5 SMELTING

2.5.1 Brief Description of Smelting Processes

2.5.1.1 Copper Smelting

The primary smelting process in the extraction of copper from its ore is a four-stage operation: (1) concentrating and drying, (2) roasting, (3) melting, and (4) oxidation converting.

These operations can and, indeed, are carried out in a number of ways depending on the characteristics of the ore and the design of the plant.

Generally, copper ore will assay at only 1.5 to 2.0% Cu. In order to reduce the volume of material to be handled through the remaining stages of smelting the first stage, or concentrating step, usually is set to yield a product of 20 to 30% Cu.

A common practice, particularly for ores high in sulfur, is a concentrating process which involves grinding and flotation followed by the three stages of smelting. The flotation concentrate is composed of copper sulfides, iron sulfides and residual gangue.

In the next process, the concentrated ore is roasted and a major portion of the sulfur is driven off leaving a product of the same materials as originally introduced to the roaster but having a substantially reduced amount of sulfur.

The temperature of the gas from the roaster may be in the range of 1200°F and the sulfur content may be from *5 to 10%*. These gas streams are cooled to around 600°F after preliminary solids collection by air dilution, water sprays or heat exchangers.

In the next step, the roasted ore is melted with an appropriate flux which produces a matte. Natural gas or oil burners oxidize the iron sulfides while silicates combine with the iron to concentrate it in the slag and thus separate the iron from the copper. Temperatures here may be around 2250°F.

Of the total sulfides in the roasted ore, *70 to 80%* ends up in the matte and *20 to 30%* in the flue gas (Environmental Engineering, 1971c). Due to the removal of a major portion of the sulfides in the roasting operation, the concentration found in the melting effluent should be less than that from the roasting operation.

In the final step, the molten matte produced in the previous process is purified by heating. This separates the iron and sulfur from the matte. No fuel is needed since the oxidation process itself supplies enough heat to maintain the converter at about 2000°F. After the separation of the slag, the sulfur is removed by oxidation yielding Cu which is approximately 99% pure.

Some typical SO_2 levels in the effluent of various processes in copper smelting are given in Table 2-24 from Environmental Engineering (1971c).

Secondary smelting or refining of copper is not a significant source of SO_2 since the copper produced originally is 99% pure.

Production of sulfuric acid is the only proven technology for removing sulfur oxides from smelter gases. Sulfuric acid production is practical from an economic standpoint only from the converter or roasting process. The more dilute gases from other operations must be incorporated since they contain more sulfur than permitted by air pollution regulations.

TABLE 2-24

SULFUR DIOXIDE EMISSIONS

	Typical SO_2 Concentrations		
Process	Copper	Zinc	Lead
Drying	0-0.5%	0-0.5%	0-0.5%
Melting (Reverb.)	0.6-2.5	--	0.0-0.2
Combined Sintering			
Updraft with recycle	--	6.0-6.5	4.0-6.0
Downdraft	--	0.1-2.4	0.8-1.8
Roaster			
Multiple hearth	5-10	4.5-6.5	--
Fluid bed	10-12	10-12	--
Coking (Blast)	--	0.08	0.01-0.25
Converting	14-21	--	--
Distillation (Retort)	--	--	--

2.5.1.2 Lead Smelting

Lead ore occurs essentially as lead sulfide (Galena). It is usually associated with zinc, iron and copper sulfides. The zinc and copper are present in recoverable amounts but frequently the iron that can be separated by mechanical means is discarded.

The ore received at the smelter has usually been concentrated by mechanical means to 50 to 70% lead, about 6% zinc, up to 4% copper, and 15 to 20% sulfur. Lead ores often contain cadmium, bismuth, gold and silver along with numerous other metals in trace amounts.

All primary lead smelters use essentially the same processing steps with minor modifications to accommodate the equipment used.

The three steps in processing concentrated lead ore are: (1) sintering, (2) reduction (usually in a blast furnace), and (3) refining.

In the sintering process, the lead sulfide ore is converted to lead oxide and sulfur.

In this operation, the sulfur dioxide may be from 4 to 6% of the effluent gas and the temperature is in the 300 to 500°F range.

The lead oxide formed in the sintering operation is reduced with coke in a blast furnace at 1800°F forming an impure metal and a slag.

In the final operation, the impure lead is refined at about 1800°F to a product which is 95 to 99% Pb. The sulfur emitted in this operation is usually less than 1%.

In most operations, the SO_2 is recovered in H_2SO_4 plants. The reported uncontrolled SO_2 emissions from lead smelting is 0.6 ton per ton of metal produced. Some typical levels of SO_2 for various lead smelting operations are shown in Table 2-24.

2.5.1.3 Zinc Smelting

Zinc ore occurs predominantly as the sulfide. Usually zinc and lead occur together in about equal amounts and a dual smelting activity may be carried on.

The ores are low in both zinc and lead content and must be concentrated before roasting. Concentrating is performed by a differential slurry flotation enriching the ore to 50 to 60% zinc, 30 to 33% sulfur, and 5 to 10% iron, with only minor quantities of copper and cadmium. The lead that co-existed is separated in the differential slurry flotation.

The second step in zinc recovery is the roasting of the concentrate which is referred to as "calcine." In this operation, most of the sulfur is driven off as SO_2. The concentration of SO_2 varies with the process, from as low as 1% to as high as 10 to 13% (see Table 2-24).

Roaster operations vary from plant to plant according to the ore and the process used in the subsequent refining operation. The temperature of the offgas may vary from 1200°F to 1900°F depending on sampling location.

The subsequent operations in zinc smelting emit some sulfur dioxide but the primary emissions are in the roasting.

The secondary production of zinc, from primary copper or lead smelters, is small compared to the amount from the ore.

2.5.2 Sampling and Analytical Results

The following operations were tested at the smelter:

Copper - roasting and reverberating
Copper - converter
Lead - total operation since the effluent from all operations was vented through a single stack

Tests were conducted with and without the fine particulate filter. Unfortunately, the only sampling positions available were following a baghouse or precipitator (see Figures 2-16 and 2-18). Thus, we could not test the methods with high particulate concentrations in the duct. With run A, SO_3 was collected by controlled condensation; run B, SO_3 was collected in isopropanol. The samples with an asterisk (*) were collected with a heated fine (0.3μ) particulate filter between the probe and SO_x train.

The sampling times ranged from 10 to 20 minutes at a rate of approximately 0.5 l/minute. Note that both the sampling rate and time were reduced because of the high SO_2 concentrations.

The SO_2 samples (at the copper roasting or reverberatory operation) were obtained with and without the fine particulate filter at two sites (A and B, see Figure 2-17) with different probes. For example, A and B represent duplicate trains, samples 1-10, 12, 14, etc. (Table 2-25) were obtained at site A without the fine filter while 11, 13, 15, etc., were obtained at site B with the filter.

The SO_2 test results for the copper smelter are given in Table 2-25. The low values, runs 10 and 12, are due to process shutdown. Some supplementary data on flue gas temperature, orsat analysis are given in Table 2-26. The SO_2 data from the lead smelter are shown in Table 2-27. Here again, the low $\sim$ 700 ppm SO_2 value was a result of the operation being shut down.

Regression analysis of the data from the copper smelter (Table 2-28) gives a high correlation coefficient and excellent regression equations for both the Ba^{++} and Ba Chlor methods with and without the fine particulate filter. Apparently the high SO_2 concentrations and the low particulate loading of this flue gas minimize the effect of the fine particulate filter. There is, however, a substantial effect of the fine filter on the CV of the barium chloranilate method. If we look at the semi-quantitative emission spectrographic analysis (Table 2-29), we see that the concentrations of zinc, calcium, and copper are reduced substantially by the filter. Atomic absorption results in Table 2-30 (on a limited number of samples) have high concentrations of Zn and Ca in the analyzed samples. These species are reduced by nearly an order of magnitude by the fine filter, hence the improvement in

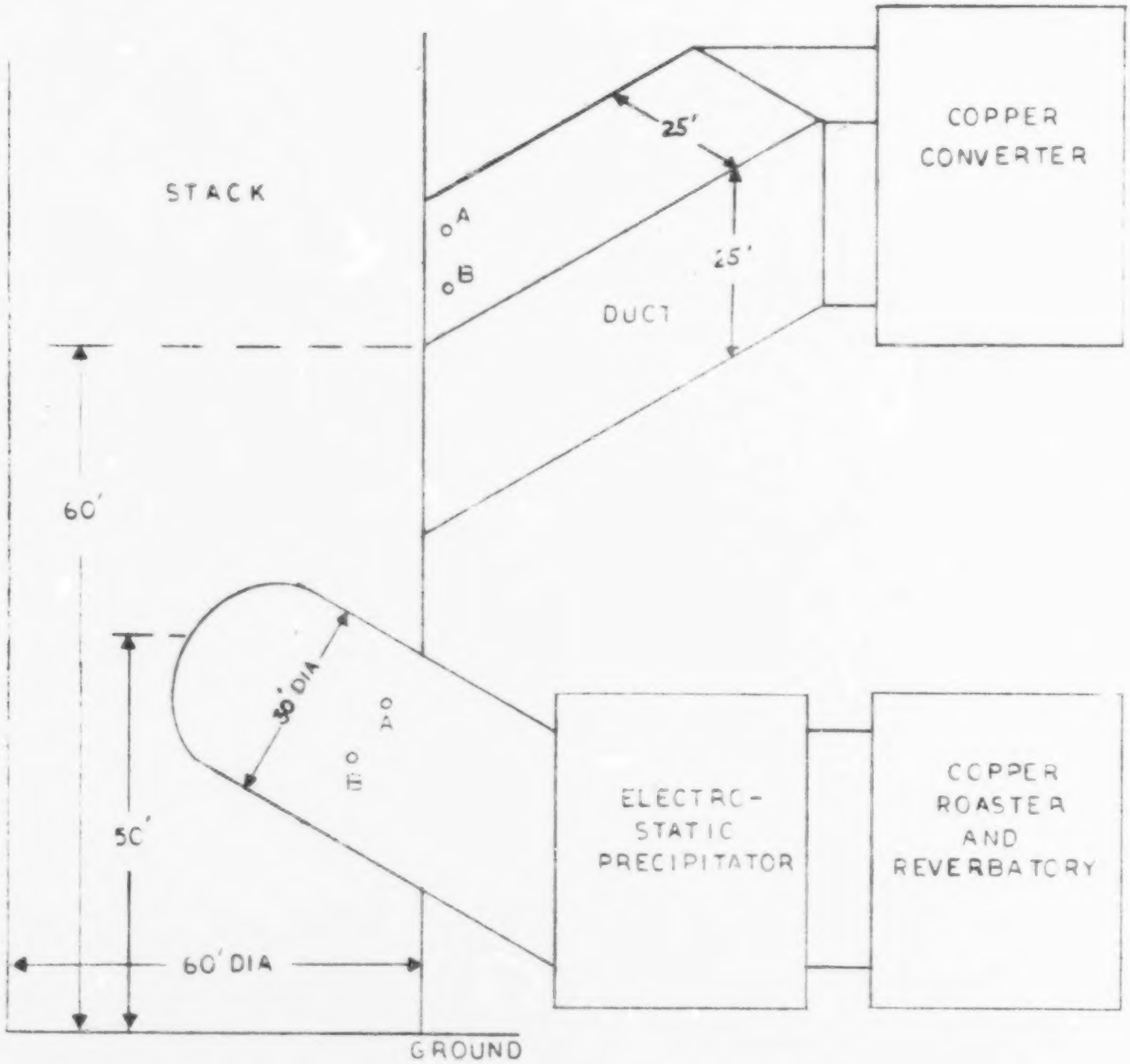

STACK
25'
25'
COPPER CONVERTER
A
B
DUCT
60'
30' DIA
A
B
50'
ELECTRO-STATIC PRECIPITATOR
COPPER ROASTER AND REVERBATORY
60' DIA
GROUND

Figure 2-16. Schematic of the Copper Smelting Operation.

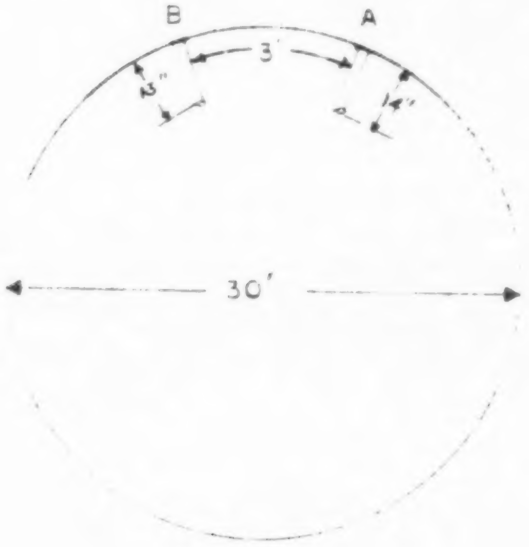


Figure 2-17. Duct Cross-Section Showing Probe Penetration (R&R) (Copper Roaster and Reverbatory).

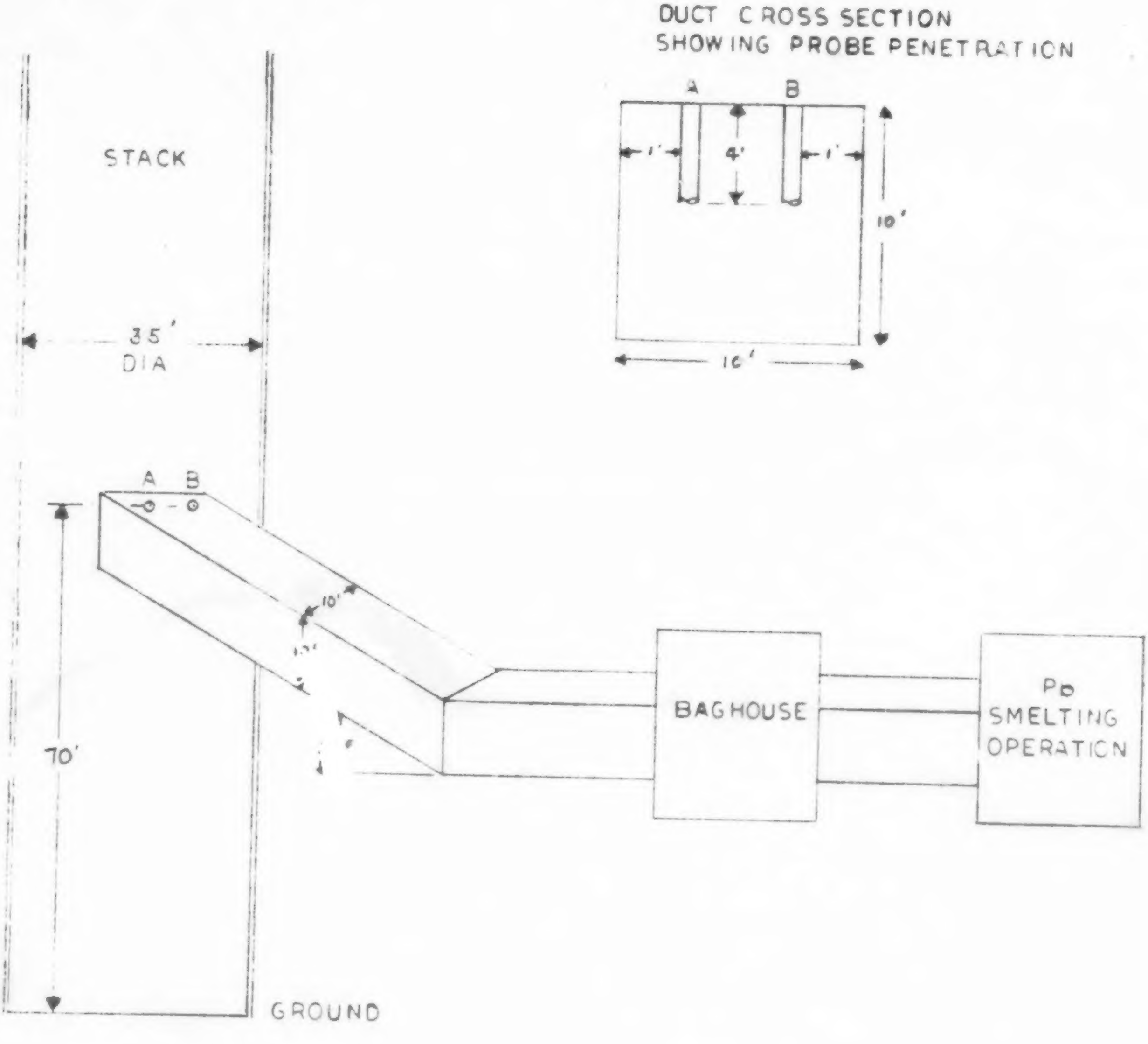

DUCT CROSS SECTION
SHOWING PROBE PENETRATION
A
B
1'
4'
1'
10'
10'
STACK
35'
DIA
A
B
10'
70'
BAGHOUSE
Pb
SMELTING
OPERATION
GROUND

Figure 2-18. Schematic of the Lead Smelting Operation.

TABLE 2-25

SO_2 TEST RESULTS FROM A COPPER SMELTER
(Roasting and Reverberatory)

Sample No.	ppm SO_2 (Ba^{++})	ppm SO_2 (Ba Chlor)
1A†	3308	4229
1B†	--	5689
2A	3447	3461
2B	3830	4038
3A	1840	2295
3B	1482	1661
4A	--	--
4B	2310	--
5A	2200	2274
5B	2229	2067
6A	4774	4821
6B	4735	4843
7A	3491	4173
7B	5438	5055
8A	3699	4750
8B	4970	5179
9A	2232	2280
9B	2693	2615
10A	106	100
10B	201	157
11A*	2395	2989
11B*	3069	3865
12A	184	237
12B	141	205
13A*	3658	3751
13B*	4249	4227
14A	--	2505
14B	--	2727
15A*	3100	3377
15B*	1562	1691
16A	2856	2755
16B	2530	2555
17A*	3376	3319
17B*	4446	4523
18A*	1980	1862
18B*	2468	2464
19A	4139	4229
19B	4112	4159
20A*	2186	2182
20B*	2738	2841

TABLE 2-25 (continued)

Sample No.	ppm SO_2 (Ba^{++})^2	ppm SO_2 (Ba Chlor)
21A	2454	2500
21B	2504	2470
22A*	3308	3383
22B*	4308	4592
23A	2430	2510
23B	2591	2724
24A*	3230	3162
24B*	5489	5369
25A	2630	2559
25B	2721	2687
26A*	5418	2995
26B*	--	--

---

*with fine particulate filter

†A and B represent results obtained in a parallel train from the same probe.

TABLE 2-26

SUPPLEMENTARY DATA FOR THE COPPER AND LEAD SMELTERS

Run No.	Date	Sampling Location	% CO_2	% O_2	Stack Temp. (°F)
1-9	2/1/72	Copper roaster and reverberatory	0.9	16.5	189
10-26	2/6/72	Copper roaster and reverberatory	1.4	15.5	225
21-32	2/7/72	Copper converter	0.0	7.5	122
33-40	2/8/72	Copper converter	0.0	5.5	153
41-56	2/9/72	Lead smelter at baghouse exit	-	-	145
57-65	2/10/72	Lead smelter at baghouse exit	-	-	162

TABLE 2-27

SO_2 TEST RESULTS FROM A LEAD SMELTER

Sample No.	ppm SO_2 (Ba^{++})	ppm SO_2 (Ba Chlor)
41A†	1071	972
41B†	--	--
42A*	1427	1445
42B*	1410	1467
43A	702	565
43B	1638	1391
44A*	1928	1710
44B*	1310	1132
45A	2172	1946
45B	4249	2985
46A*	4430	4642
46B*	4841	3430
47A	2995	2740
47B	5031	3462
48A*	3160	2948
48B*	2935	2741
49A	631	110
49B	842	521
50A*	2172	2037
50B*	--	--
51A	2400	2131
51B	4076	3616
52A*	4822	4696
52B*	--	--
53A	2508	2250
53B	3991	4059
54A*	5253	4982
54B*	5014	4898
55A	2581	2209
55B	2320	2219
56A*	5357	5140
56B*	5218	5140
57A	2347	2491
57B	4197	4185
58A*	4554	4461
58B*	3901	3890
59A	2696	2525
59B	4368	4310
60A*	4400	4301
60B*	4168	4229
61A	2205	2050
61B	--	--

TABLE 2-27 (continued)

Sample No.	ppm SO_2 (Ba^{++})	ppm SO_2 (Ba Chlor)
62A*	4368	4434
62B*	4249	4376
63A	2480	2353
63B	3527	3532
64A*	4066	4131
64B*	3230	3173
65A	2631	2585
65B	2519	2492

---

[*] with fine particulate filter

[+] A and B represent results from a parallel train run off the same probe.

TABLE 2-28

STATISTICAL ANALYSIS FOR SO_2 TEST RESULTS FROM SMELTERS

Site	Run No.	Regression Equation	Correlation Coefficient	Coefficient of Variation of Analytic Method	Mean
Cu Roaster and Reverbatory	1-26*	ppm Ba Chlor = 1.02 ppm Ba^{++} + 95	0.98		
	1-26*			(Ba^{++}) 1.8%	3080
	1-26*			(Ba Chlor) 6.5	3360
	1-26†	ppm Ba Chlor = 0.99 ppm Ba^{++} + 196	0.95		
	1-26†			(Ba^{++}) 1.6%	3351
	1-26†			(Ba Chlor) 1.8	3298
Pb Smelter	41-65*	ppm Ba Chlor = 0.89 ppm Ba^{++} + 28	0.95		
	41-65*			(Ba^{++}) 4.0%	3139
	41-65*			(Ba Chlor) 9.0	2841
	41-65†	ppm Ba Chlor = 0.96 ppm Ba^{++} + 13	0.96		
	41-65†			(Ba^{++}) 1.5%	4232
	41-65†			(Ba Chlor) 7.7	3490

---

*With just glass wool filter

†With fine particulate filter and glass wool filter

TABLE 2-29

SEMIQUANTITATIVE EMISSION SPECTROGRAPHIC ANALYSIS OF SO_2
IMPINGER SAMPLES FROM SMELTING OPERATIONS

	ppm Al	ppm B	ppm Be	ppm Cu	ppm Cr	ppm Fe	ppm Mg	ppm Mn	ppm Ni
Cu Smelter (no filter)	0.03-0.3	--	--	0.3-3	0.03-0.3	0.1-1	0.03-0.3	0.001-0.01	0.01-0.1
Cu Smelter (with filter)	0.03-0.3	--	--	0.1-1	0.003-0.03	0.03-0.3	0.03-0.3	0.001-0.01	0.003-0.03
Pb Smelter (no filter)	0.03-0.3	--	--	0.1-1	0.03-0.3	0.3-3	0.03-0.3	0.003-0.03	0.03-0.3
Pb Smelter (with filter)	0.03-0.3	--	--	0.1-1	0.01-0.1	0.1-1	0.03-0.3	0.001-0.01	0.003-0.03

	ppm Ag	ppm Pb	ppm Sn	ppm Ca	ppm Si	ppm Ti	ppm Zn	ppm Na
Cu Smelter (no filter)	0.1-1	0.03-0.3	--	0.3-3	0.03-0.3	0.01-0.1	0.1-1	0.3-3
Cu Smelter (with filter)	0.1-1	0.03-0.3	0.03-0.3	0.03-0.3	0.03-0.3	0.01-0.1	0.03-0.3	0.3-3
Pb Smelter (no filter)	0.1-1	0.1-1	0.03-0.3	0.03-0.3	0.03-0.3	0.003-0.03	0.03-0.3	0.1-1
Pb Smelter (with filter)	0.03-0.3	0.1-1	--	0.03-0.3	0.03-0.3	0.003-0.03	0.03-0.3	0.1-1

TABLE 2-30

ATOMIC ABSORPTION RESULTS FROM ANALYSIS OF SO_2 IMPINGER LIQUID FROM COPPER AND LEAD SMELTING

Source	ppm (μg/ℓ) Ca	Zn	Na	Cu[*]	Remarks
Copper Smelter	105	105	<30[†]	<2	No fine filter
	<20	<3.5	<30	<2	With fine particulate filter
Lead Smelter	<20	5	70	6	No fine filter
	<20	5	<30	6	With fine particulate filter

---

[*] By emission spectroscopy

[†] The relatively higher (30 ppm) detection limits are due to the small volume of stack gas sampled (<10ℓ).

CV of barium chloranilate. No significant quantities of Na are present, therefore, Ba^{++} is not affected.

The SO_2 results for the lead smelting operation are given in Table 2-27. Here, the fine particulate filter does improve the agreement between the two methods slightly. The regression slope is 0.89 without the filter and 0.96 with the filter as indicated in Table 2-28. The correlation coefficients do not change appreciably. The CV's indicate an interference with the Ba^{++} titration which is removed by filtration. Atomic absorption results in Table 2-30 show that the Na concentration is reduced considerably between a filtered and unfiltered SO_2 sample. This may very well account for the improved precision with the Ba^{++} titration. The Ba Chlor method, however, shows a considerable interference which is only slightly diminished with the filter. From the data in Table 2-30, the trace amounts of both Zn and Cu are present at about the same concentration in filtered and unfiltered samples. This could account for the interference.

In order to check the accuracy of the spectrographic analysis, some SO_2 impinger samples were analyzed with a Cu electrode. Chloride was added to decompose the residual H_2O_2 prior to analysis. Two filtered samples from the Cu smelter gave 0.07 and 0.1 ppm Cu^{++} for the emission spectrographic range 0.1 to 1 and several unfiltered samples gave 0.26 and 0.82 ppm Cu^{++} for the spectrographic range 0.3 to 3. The agreement between the two methods indicates that the emission spectrographic concentrations are in the right range. We should point out, however, that only a single sample (filtered and unfiltered) were sent out for analysis. Therefore, these data may not be representative of the actual concentration.

SO_3 samples were collected at the smelting operations by controlled condensation and 80% IPA absorption. The 80% IPA samples were flushed with air (passed through a charcoal column) at a rate of approximately 3 l/min for 10 minutes. The *condenser and IPA* SO_3 *samples* were analyzed for sulfate by the barium chloranilate method. The results selected for inclusion in Table 2-31 were those where the SO_2 values for trains A and B were nearly equal. For example, if the SO_2 values differed by 50%, this might indicate a leak in one of the trains, thus, these data would not be valid and were not used.

TABLE 2-31

SO_3 TEST RESULTS FROM Cu AND Pb SMELTING OPERATIONS

ppm SO_3 Controlled Condensation[*]	80% IPA Absorption[*]	Source
30	11	Cu Smelting
6	11	Cu Smelting
4	15	Cu Smelting
17	5	Cu Smelting
8	10	Cu Smelting
10	10	Cu Smelting
2	10	Cu Smelting
7	6	Cu Smelting
4	10	Cu Smelting
6	8	Cu Smelting
11	30	Cu Smelting
11	32	Cu Smelting
11	19	Cu Smelting
17	22	Cu Smelting
1	23	Cu Smelting
15	23	Cu Smelting
1	9	Pb Smelting
7	10	Pb Smelting
3	12	Pb Smelting
1	6	Pb Smelting
10	9	Pb Smelting
1	8	Pb Smelting
8	12	Pb Smelting
1	8	Pb Smelting

---

[*] Collected in parallel trains from the same probe

The mean SO_3 values for the controlled condensation and IPA are 7.4 and 12.5 ppm, respectively. The regression analysis obtained is:

$$\text{ppm } SO_3 \text{ (IPA)} = 10.2 + 0.3 \text{ ppm } SO_3 \text{ (controlled condensation)}$$

with a correlation coefficient of only 0.30. The IPA is very susceptible to interference (oxidation of dissolved SO_2) because of the high concentration of SO_2 in the effluent and the presence of metals (catalysts) in the sample. Note that low SO_3 values would be expected due to the stack temperature (~ 140°F) and the sampling site, e.g., after particulate collection device.

The SO_2 test results on the copper (roasting and reverberatory) smelter vary from approximately 2000 to 5000 ppm. The CO_2 and O_2 analyses in Table 2-26 for this operation indicate dilution with approximately 5 volumes of air. On this basis, the SO_2 values would be approximately 1-2.5% SO_2. This is in reasonable agreement with the predicted values in the previous section (Table 2-24). The emissions are highly variable. If we consider the reverberatory firing rate in Table 2-32, we note that a 50% drop was recorded between 11 and 10 o'clock on 2/1. The average SO_2 concentration dropped from approximately 3700 ppm to approximately 1700 ppm. However, with a constant firing rate all afternoon, the SO_2 increased from 2000 to 5000 ppm and dropped back down again. Thus, one cannot correlate these results with the firing rate since the SO_2 depends on variables such as percent sulfur in the ore, the time during the cycle, etc. The low values, samples 10 and 12, represent periods when the smelter was shut down during the actual sampling period. There appeared to be some problems with the sampling trains leaking (#15, 24, etc.) on the copper (R&R) stack but the system could not be leak-tested without removing the probe from the duct. The probe was leak-tested each day. It would have been difficult and time-consuming to leak-test the system between runs.

The fourteen runs at the copper converter (where the CuS produced in the reverberatory operation is converted to SO_2 and Cu) yielded SO_2 concentrations less than 100 ppm for both Ba^{++} and Ba Chlor. Since this operation accounts for the major portion of SO_2 emissions from Cu smelters, the data are certainly not typical of expected levels (SO_2 concentrations from

TABLE 2-32

LOG OF OPERATIONS FOR COPPER SMELTER

REVERB AND ROASTER FLUE

Date	Time	Roasters Operating	Reverb Furnace Firing Rate
2/1	10:30 a.m. - 11:11 a.m.	4	150,000 CFH
	1:45 p.m. - 4:00 p.m.	2	70,000 CFH
	4:00 p.m. - 4:32 p.m.	2	65,000 CFH
2/6	12:04 p.m. - 1:52 p.m.	4	135,000 CFH
	1:52 p.m. - 2:40 p.m.	2	135,000 CFH
	2:40 p.m. - 3:05 p.m.	2	100,000 CFH
	3:05 p.m. - 5:30 p.m.	2	90,000 CFH

CONVERTER FLUE

Date	Time	Converters Operating
2/7	10:56 a.m. - 11:45 a.m.	1 converter
	1:40 p.m. - 2:00 p.m.	1 converter
2/8	7:40 a.m. - 8:10 a.m.	2 converters
2/8	8:26 p.m. - 9:57 p.m.	3 converters

LOG OF OPERATIONS FOR LEAD SMELTER

		Roasters Operating	
Date	Time	1st Stage	2nd Stage
2/9	1:20 - 1:50 p.m.		1
	3:00 - 3:40 p.m.	2	
	3:40 - 4:35 p.m.		1
	5:25 - 5:40 p.m.	2	1
	5:40 - 11:00 p.m.	4	2
2/10	8:30 - 10:45	4	2

~ 1.5-8% were expected). Orsat analysis of flue gas samples taken through the probe yielded O_2 values which were from 5.5-7.5% and CO_2 values of 0%. The negligible CO_2 values are reasonable since no auxiliary fuel is used in this operation. During the testing period (10:00 a.m. to 1:00 p.m. on 2/7 and 7:00 to 10:00 a.m. on 2/8), one to four converters were running. Thus, the low SO_2 values cannot be explained on the basis of the process not operating or a broken or leaky probe.

2.5.3 Conclusions

The utilization of a fine particulate filter in the sampling train at the copper smelter improved the precision of the barium chloranilate method considerably. A measurable effect on CV was not observed with the barium titration and no problem was noted with the endpoint of the titration (filtered or unfiltered) since the SO_2 concentrations were very high. On the lead smelter, however, the fine particulate filter improved the CV of the barium ion titration. This was attributed to the presence of sodium in the samples without the fine particulate filter. No change in precision was seen for the barium chloranilate. Atomic absorption results indicated traces of Cu and Zn at about the same level in the samples with and without the fine particulate filter. The SO_3 concentrations by the controlled condensation method are ~ 1/2 the values obtained by 80% IPA absorption. The controlled condensation values seem more reasonable because the stack temperature is so low and the sampling location follows a particulate collector. The IPA values are higher due to oxidation of dissolved SO_2.

The fine particulate filter does improve the analytical results for Cu and Pb smelters even when the particulate concentrations are low, e.g., after an electrostatic precipitator or baghouse.

2.6 SULFURIC ACID PRODUCTION

2.6.1 Brief Description of Sulfuric Acid Plants

Sulfuric acid manufacture is, by far, the largest industrial chemical process. Production in 1967 amounted to 28,800,000 tons (MCA and U.S.P.H.S., 1965). Approximately 97% was produced by the contact process, and the remainder by the chamber process. The latter process is rapidly decreasing in importance, in 1963, chamber process acid accounted for about 97% of the total (MCA and U.S.P.H.S., 1965). Both processes are potential sources of both sulfuric acid mist (SO_3 or H_2SO_4) and sulfur dioxide gas (SO_2). The chamber process also releases nitrogen oxides.

Flow diagrams of the chamber and contact processes are shown in Figures 2-19 and 2-20, respectively. In both processes, the principal point of emissions is the exit stack from the final absorption tower, the Gay-Lussac tower (chamber) or the final absorber (contact). The pollutant species in the tail gas stream are indicated at the right of each figure.

Uncontrolled emissions of SO_2 range from 1000 to 2000 ppm (by volume) in the chamber process and from 1000 to 6000 ppm in the contact process (EPA, 1971). This is equivalent to about 15 to 85 pounds of SO_2 per ton of acid (100% H_2SO_4) produced (EPA, 1971). Emissions of acid mist range from 5 to 30 milligrams per cubic foot in the chamber process (EPA, 1971). The efficiency of the final absorption step is generally higher in the contact process, so that acid mist emissions tend to be lower, 3 to 15 milligrams per cubic foot (EPA, 1971). Excursions to about 50 milligrams per cubic foot have been reported (EPA, 1971a). The normal range of emissions corresponds to an output of approximately 0.5 to 3 pounds of acid mist (H_2SO_4) per ton of acid produced.

The Federal Standards of Performance for new stationary sources (EPA, 1971a) require significantly lower emission levels for both SO_2 and acid mist than are customarily found in uncontrolled plants. For SO_2, the standard limits emissions to 4 lb per ton of acid produced, and for acid mist, 0.15 lb per ton of acid produced, both averaged over two hours.

Control processes for SO_2 generally consist of utilizing additional absorbers (dual-absorption plants). In such plants, the SO_2 levels range from about 90 to 250 ppm (EPA, 1971a) or from 1.2 to 3 lb per ton of acid produced. Alternatively, tail gas scrubbing with sodium sulfite-bisulfite can be used to reduce SO_2 emissions with essentially equivalent results.

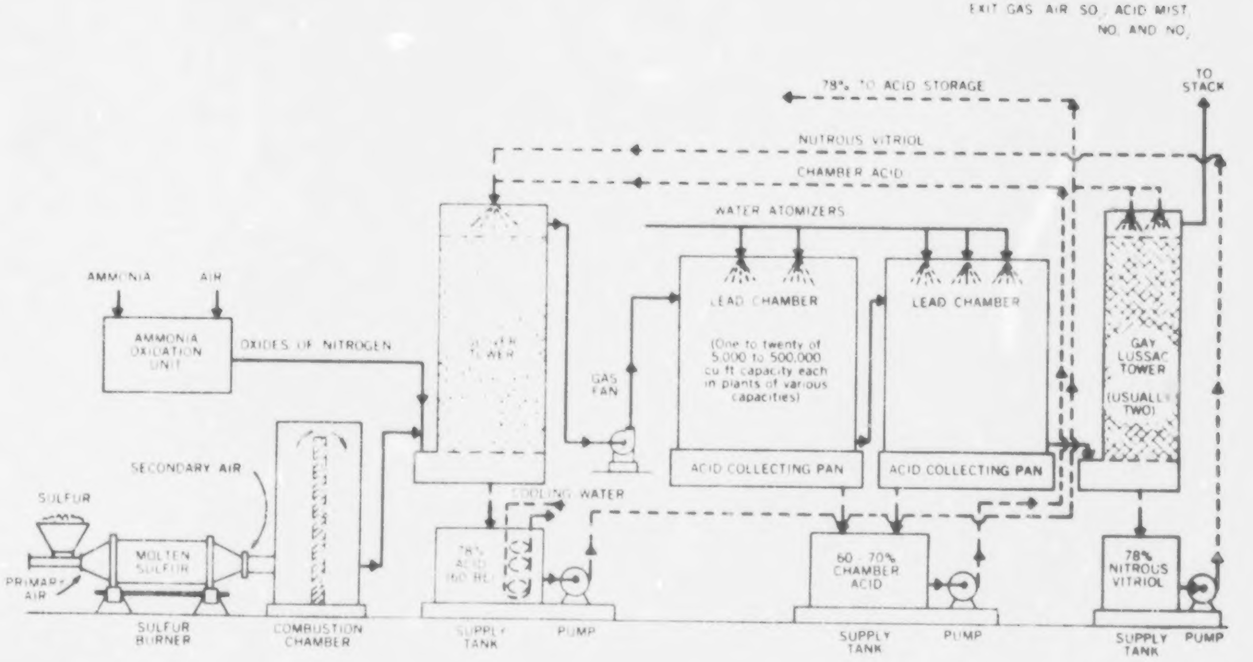
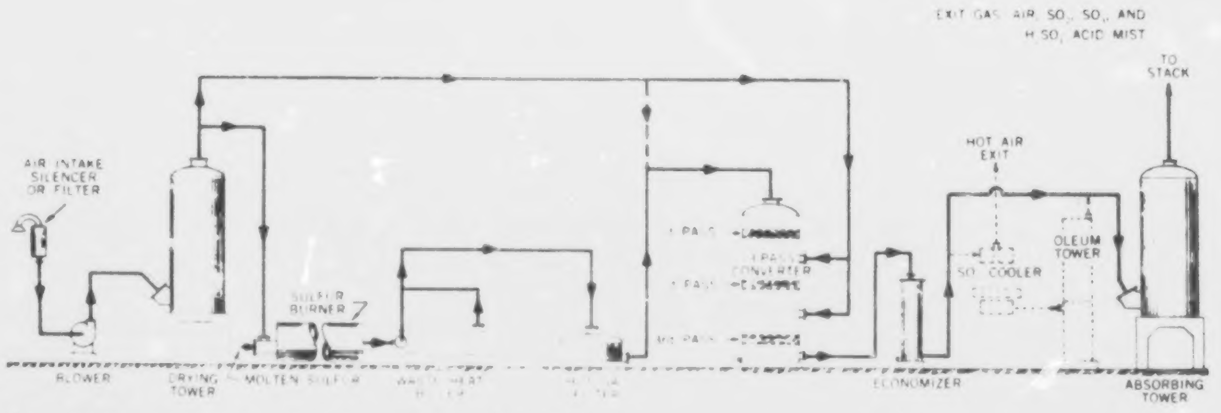

EXIT GAS AIR SO_2 ACID MIST NO AND NO_2
TO STACK
78% TO ACID STORAGE
NUTROUS VITRIOL
CHAMBER ACID
WATER ATOMIZERS
AMMONIA
AIR
AMMONIA OXIDATION UNIT
OXIDES OF NITROGEN
GLOVER TOWER
GAS FAN
LEAD CHAMBER
(One to twenty of 5,000 to 500,000 cu ft capacity each in plants of various capacities)
LEAD CHAMBER
GAY LUSSAC TOWER
(USUALLY TWO)
ACID COLLECTING PAN
ACID COLLECTING PAN
SECONDARY AIR
SULFUR
MOLTEN SULFUR
PRIMARY AIR
SULFUR BURNER
COMBUSTION CHAMBER
COOLING WATER
78% ACID (60 Bé)
SUPPLY TANK
PUMP
60 - 70% CHAMBER ACID
SUPPLY TANK
PUMP
78% NITROUS VITRIOL
SUPPLY TANK
PUMP

Figure 2-19. Simplified Flow Diagram of Typical Lead-Chamber Process for Sulfuric Acid Manufacture (Based on Use of Elemental Sulfur as the Raw Material).

From MCA and U.S.P.H.S. (1965).


EXIT GAS: AIR, SO2, SO3, AND
H2SO4 ACID MIST
TO STACK
AIR INTAKE SILENCER OR FILTER
SULFUR BURNER
HOT AIR EXIT
1ST PASS
3 PASS CONVERTER
2ND PASS
3RD PASS
SO3 COOLER
OLEUM TOWER
BLOWER
DRYING TOWER
MOLTEN SULFUR
WASTE HEAT BOILER
HOT GAS FILTER
ECONOMIZER
ABSORBING TOWER

(When four-pass converter is used, cooling after both second and third passes is done by air quench.)

Figure 2-20. Gas Flow Diagram for Typical Sulfur-Burning Contact Plant in which Air Quench is Used for Part of Converter Interstage Cooling.

Acid mist control can be achieved by demisting with high efficiency fiber filters or electrostatic precipitators. Typical data on the performance of fiber mist eliminators is given in Table 2-33 (EPA, 1971). In both cases, the emissions can be reduced to about 0.1 pound per ton (EPA, 1971a). This is equivalent to a concentration of about 0.5 mg per standard cubic foot. Measurements of acid mist in the effluent of plants where SO_2 controls have been installed, indicate that the additional absorption can reduce acid mist to levels below the emission standard (EPA, 1971a).

2.6.2 Sampling and Analytical Results

The sampling train utilized in the sulfuric acid plant was the conventional EPA SO_2 train. No probe was used in the tests. The impingers were attached to a gate valve which penetrated approximately 6 inches into the duct (see Figure 2-21). The plant layout is given in Figure 2-21. The test results for the sulfuric acid plant are shown in Table 2-34. For runs 1-15, two or three SO_x trains (A and B or A, B and C) were run in parallel off the gate valve. All the SO_3 up to run 57 was collected by absorption in 80% isopropanol. Some were analyzed by barium chloranilate and others were analyzed by barium ion titration as indicated. The "C" trains were usually (but not always) run with solid sorbents in front of the SO_2 impingers. The low SO_2 values, 20 to 300 ppm, were obtained with the solid sorbents* in the train while the high SO_2, approximately 1000 ppm, represent runs with the conventional EPA train (IPA plus peroxide impingers for collection of SO_3 and SO_2, respectively).

The sampling rate was 1.0 l/min for approximately 15 to 30 minutes. Statistical analysis of the SO_2 data in Table 2-34 (runs 1-57) gives

$$\text{ppm } SO_2 \ (Ba^{++}) = +32.6 + 0.97 \text{ ppm } SO_2 \ (\text{Ba Chlor})$$

with a correlation coefficient of 0.96. No problems (interferences) were observed with the conventional EPA train. The SO_3 data were split into those analyses which were done by the two analytical methods and the following

---

*These results will be discussed in detail in Appendix C.

TABLE 2-33

COLLECTION OF H_2SO_4 MIST FROM A SULFUR-BURNING CONTACT SULFURIC ACID PLANT WITH FIBER MIST ELIMINATORS

Contact plant production	Mist loading[a] of gases leaving absorber and entering mist eliminator, mg H_2SO_4/scf	Mist loading[a] of gases leaving mist eliminator, mg H_2SO_4/scf	Particle collection efficiency (3μ and smaller), %
	Mist Eliminator A[b]		
99% H_2SO_4 and 65% oleum at full capacity	30.9	1.50	95.1
	31.8	1.43	95.3
	39.9	1.64	95.9
99% H_2SO_4 and 25% oleum at 75% capacity	6.55	0.124	98.1
	8.75	0.169	98.1
	6.64	0.125	98.1
	Mist Eliminator B[b]		
99% H_2SO_4 and 25% oleum at full capacity	14.4	0.085	99.4
	18.3	0.112	99.4
	19.3	0.095	99.5
99% H_2SO_4 and 25% oleum at 60% capacity	6.88	0.045	99.3
99% H_2SO_4 at 60% capacity	2.12	0.014	99.3

[a] The mist-loading values are limited to particles 3 microns in diameter and smaller.

[b] Mist eliminator A was designed for 100 percent efficiency for particles larger than 3 microns diameter and for 95 percent efficiency for particles 3 microns and smaller, operated at a pressure drop of 3 inches of water. Mist eliminator B was designed for 100 percent efficiency for particles larger than 3 microns and for 99 percent efficiency on particles 3 microns diameter and smaller, operated at a pressure drop of 6 inches of water.

From MCA (1965).

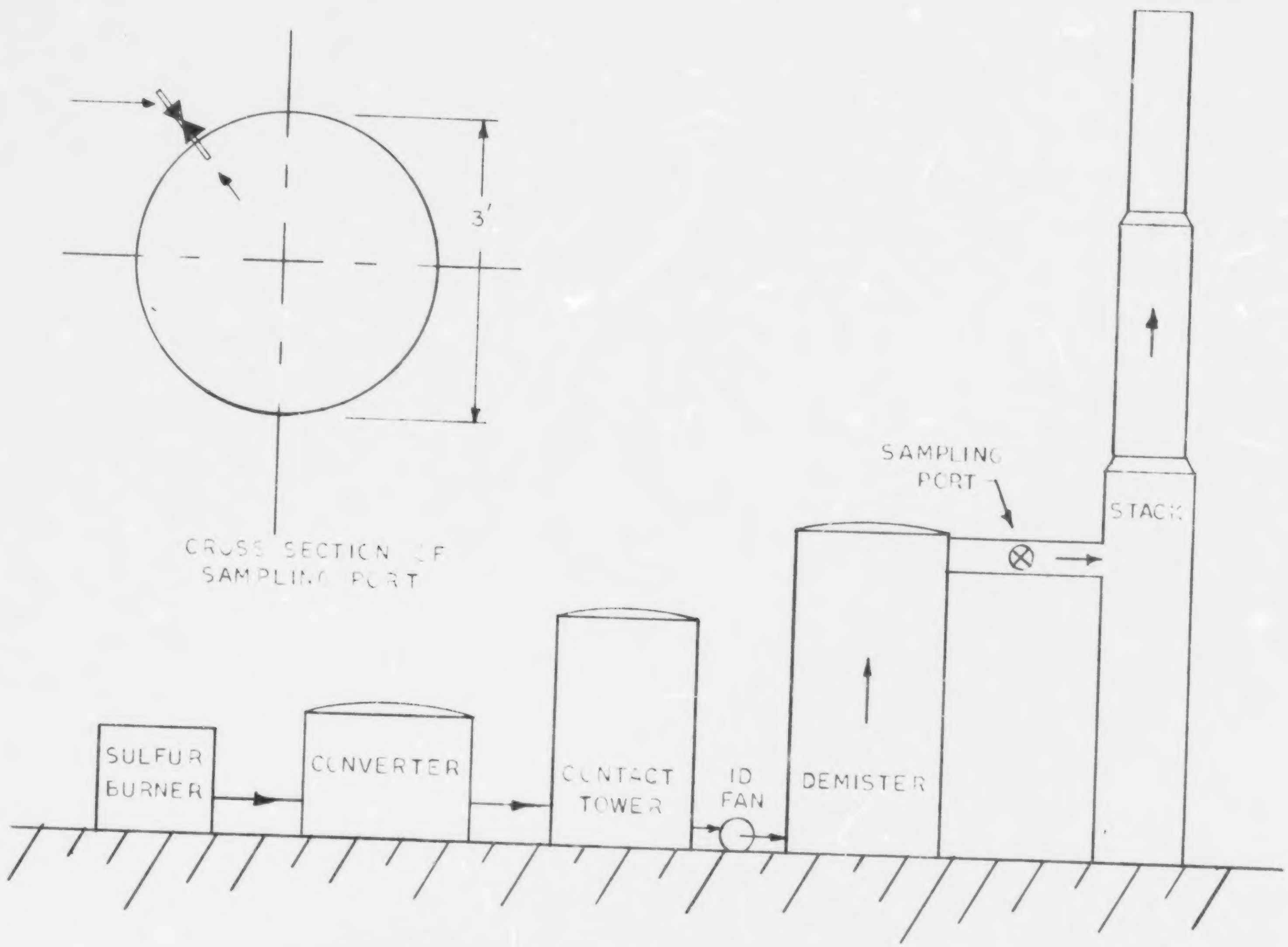

CROSS SECTION OF
SAMPLING PORT
3'
SAMPLING
PORT
STACK
SULFUR
BURNER
CONVERTER
CONTACT
TOWER
ID
FAN
DEMISTER

Figure 2-21. Sulfuric Acid Plant Layout.

TABLE 2-34

SO_2 AND SO_3 TEST RESULTS FROM A SULFURIC ACID PLANT

Sample No.	ppm SO_2 (Ba Chlor)	ppm SO_2 (Ba^{++})	ppm SO_3 (Ba Chlor)
1A	1130	1108	23
1B	1136	1086	33
2A	1177	1112	37
2B	1189	1107	21
3A	1080	1049	46
3B	1122	1049	23
4A	1026	1002	74
4B	987	876	109
4C[††]	68	12	--
5A	1159	1006	6
5B	1101	1080	15
5C[††]	0	8	--
6A	1080	1078	21
6B	1110	1078	21
6C	1097	1088	19
7A	1089	1135	21
7B	1099	1104	24
7C	1115	1130	23
8A	1048	1082	26
8B	1026	1092	25
8C	1035	1096	32
9A	1155	1210	22
9B	1188	1218	18
9C	1179	1206	25
10A	1186	1170	20
10B	1171	1169	20
10C	1179	1216	15
11A	1163	1150	13
11B	1160	1180	8
11C	1151	1172	14
12A	829	1044	53
12B	865	1080	5
12C	1055	1066	48
13A	1082	1110	41
13B	1098	1090	18
13C	1061	1114	34
14A	1096	1113	32
14B	1007	1078	18
14C	1103	1111	39
15A	1188	1113	37
15B	1249	1035	26
15C	848	947	46

TABLE 2-34 (continued)

Sample No.	ppm SO_2 (Ba Chlor)	ppm SO_2 (Ba^{++})	ppm SO_3 (Ba Chlor)
16A	765	882	19
16B	1193	1173	19
16C††	151	199	--
17A	1145	1167	27
17B	893	890	21
17C††	172	101	--
18A	1178	1143	23
18B	1149	1125	22
18C††	243	109	--
19A	1192	1133	5
19B	1199	1097	7
19C††	117	79	--
20A	1171	1153	11
20B	1182	1107	48
20C††	211	115	--
21A	1228	1158	4
21B	1261	1321	4
21C	1202	881	48
22A	1117	1062	24
22B	965	1025	31
22C††	65	59	--
23A	1182	1161	26
23B	2385	1104	21
23C††	40	53	--
24A	1212	1120	6
24B	1085	1097	--
24C††	10	73	--
25A	1032	1054	21
25B	1191	1141	17
25C††	15	56	--
26A	1136	1137	14
26B	1118	1115	20
26C††	30	37	--
27A	1128	1137	18
27B	1135	1149	15
27C	1103	1188	16
28A	990	1041	8
28B	935	1014	10
28C	1001	1069	17
29A	1093	1097	7
29B	993	1104	--
29C	1018	1130	--
30A	1029	1141	48†
30B	1056	1135	54†
30C	1186	1188	47†
31A	1250	1225	47†
31B	1127	1166	55†
31C	972	1053	59†

TABLE 2-34 (continued)

Sample No.	ppm SO_2 (Ba Chlor)	ppm SO_2 (Ba^{++})	ppm SO_3 (Ba^{++})
32A	1227	1259	52
32B	1247	1261	68
32C	1300	1292	54
33A	1340	1255	16
33B	1348	1277	18
33C	1654	1275	34
34A	1463	1487	19
34B	1270	1226	28
34C	1193	1258	34
35A	1108	1109	28
35B	1166	1181	24
35C	1113	1120	34
36A	555	430	1356
36B	962	1090	29
36C	699	1084	35
37A	692	800	30
37B	1006	1178	37
37C	859	1232	33
38A	1791	1759	50
38B	1255	1145	36
38C	1090	1149	39
39A	1087	1245	40
39B	1065	1174	49
39C	1033	1191	65
40A	986	1103	29
40B††	38	31	21*
40C	687	827	32*
41A	1050	1127	35
41B††	74	70	5473
41C	1038	1315	61
42A	1045	1090	46
42B	972	1012	76*
42C	1112	1259	32*
43A	1098	1231	48*
43B	1143	1225	47
43C	111	123	--
44A	922	351	376
44B	1116	1219	43
44C††	53	69	--
45A	1170	1193	7
45B	1141	1214	12
45C††	18	90	--
46A	757	653	--
46B	1350	1325	--
46C††	38	144	--

TABLE 2-34 (continued)

Sample No.	ppm SO_2 (Ba Chlor)	ppm SO_2 (Ba^{++})	ppm SO_3 (Ba^{++})
47A	1170	1106	163
47B	1089	53	235
47C††	32	87	--
48A	1135	1137	89
48B	1144	1139	39
48C††	25	75	--
49A	1064	1076	33
49B	1055	1085	23
49C††	305	93	--
50A	1112	1133	29
50B	1036	1145	28
50C††	36	144	--
51A	1081	1205	28
51B	1111	1145	23
51C††	22	81	--
52A	1243	1235	49
52B	1234	1266	41
52C††	--	83	--
53A	930	1236	35
53B	1164	1246	19
53C††	40	87	--
54A	945	1315	48
54B	1158	1223	40
54C††	82	105	--
55A	1170	1105	68
55B	1161	1242	81
55C††	104	95	--
56A	1139	1215	24
56B	1156	1208	22
56C††	--	62	--
57A	941	1063	45
57B	1089	1147	10
57C††	102	41	--

---

[*] Sample analyzed by barium chloranilate method.

[†] Sample analyzed by barium titration method.

[††] Represents amount collected in peroxide impingers following a solid sorbent cartridge (see Appendix C).

statistical results were obtained:

Runs 1-29, Ba Chlor Analysis:

$$\text{ppm } SO_3 \text{ (IPA Train B)} = -2.4 + 1.03 \text{ ppm } SO_3 \text{ (IPA Train A)}$$

Correlation coefficient = 0.80

Runs 30-57, Ba^{++} Titration:

$$\text{ppm } SO_3 \text{ (IPA Train B)} = -1.8 + 1.06 \text{ ppm } SO_3 \text{ (IPA Train A)}$$

Correlation coefficient = 0.87

The SO_2 values for the two methods were in good agreement as expected. The SO_3 data showed good agreement for both analytical methods when 80% IPA was used in both trains. The high correlation coefficients and near unity slopes are considerably better than any previous SO_3 comparisons when IPA was run versus the controlled condensation method. Thus, the problem is not the analytical method.

The SO_2 and SO_3 data in Table 2-35 were obtained approximately one month later than that reported in Table 2-34. These data were collected to obtain some comparison between IPA and controlled condensation collection of SO_3 for a sulfuric acid plant. *All the samples* (SO_2 and SO_3) *were analyzed by barium ion titration*. The statistical analysis obtained was:

$$\text{ppm } SO_2 \text{ (Train B)} = +3.3 + 0.99 \text{ ppm } SO_2 \text{ (Train A)}$$

Correlation coefficient = 0.99

$$\text{ppm } SO_3 \text{ (controlled condensation)} = 0.13 + 0.45 \text{ ppm } SO_3 \text{ (IPA)}$$

Correlation coefficient = 0.80

These data indicate that the SO_3 data by controlled condensation produce considerably lower SO_3 values (note slope of 0.45) than IPA although the SO_2 data on the same trains produce high correlations and a unity slope. This is essentially the same as seen for power plants and smelting operations where other comparisons were conducted for SO_3.

TABLE 2-35

SO_2 AND SO_3 TEST RESULTS FROM A SULFURIC ACID PLANT

Sample No.	Train a*		Train b†	
	ppm SO_2	ppm SO_3	ppm SO_2	ppm SO_3
59	840	5	622	4
60	893	10	885	6
61	868	6	890	4
62	911	4	925	1
63	889	7	849	3
64	887	5	923	2
65	772	3	802	3
66	855	4	875	1
67	907	1	904	4
68	942	6	941	1
69	961	7	889	2
70	797	3	864	1
71	680	6	833	2

---

[*] SO_3 collected in impingers containing 80% IPA

[†] SO_3 collected by condenser

SO_2 collected in H_2O_2 in all trains

2.6.3 Conclusions

The EPA sampling train and both the barium ion titration and barium chloranilate methods yield reliable data without any modification.

A considerable discrepancy exists between the controlled condensation and 80% isopropanol absorption methods for SO_3 collection. This should be investigated in detail.

2.7 RECOMMENDATIONS FOR FUTURE WORK

In Section 1, we have seen that the SO_3 results from the controlled condensation method and IPA absorption methods differ considerably. The correlation coefficients which vary from 0.1 to 0.4 for the field samples are very poor. Laboratory work with *only* SO_2 added to the pilot plant effluent fired on gas indicates that SO_2 is soluble in IPA to the extent of $\sim$ 100 ppm (at ice temperatures). This is consistent with the field test data for coal-oil combustion where train c which not flushed gave SO_2 values about 100 ppm lower than train b where the SO_2 was removed by flushing. The laboratory studies indicated that after 15 minutes of flushing the IPA impingers with air, the $SO_4^=$ background was reduced from 20% (100 ppm) to a minimum value of 1-2%. It is interesting that the SO_3 values typically found are about 1-3% of the SO_2 values. We appear to be getting conversion to sulfate although no trace metals are present in the effluent.

In Section 2 we find results for SO_3 similar to those in Section 1. The condenser train has little correlation with the SO_3 collected in the IPA. We have not done enough laboratory work to establish which collection technique gives the correct SO_3 values although the absorption in IPA is probably subject to more errors as a result of catalytic oxidation of the dissolved SO_2.

We recommend that additional laboratory and field studies be conducted to determine the best method for collection of SO_3.

REFERENCES

Cowan, S., "Sulfur Balance on a Gray Iron Foundry," American Foundrymen's Society Meeting (May 1971).

Danielson, J., Ed., "Air Pollution Engineering Manual," U.S. Dept. HEW, Pub. #999-AP-40 (1967).

Driscoll, J. N. and A. W. Berger, "Improved Chemical Methods for Sampling and Analysis of Gaseous Pollutants from the Combustion of Fossil Fuels," Vol. I, Sulfur Oxides, APTD #1106 (1971).

Driscoll, J. N., J. H. Becker and J. F. McCoy, "Assistance to Southwest Research Institute on a Collaborative Testing Program," Subcontract under EPA Contract No. CPA 70-40 (1972).

EPA, "Standards of Performance for New Stationary Sources," Federal Register (Dec. 23, 1971).

Environmental Engineering, "Background Information for Establishment of National Standards of Performance for New Sources," for EPA under Contract No. CPA 70-142, Gray Iron Foundries (1971), Kraft Mills (1971a), Iron and Steel (1971b), Smelting (1971c).

Galeano, S. F., T. W. Tucker and L. Duncan, "Determination of Sulfur Oxides in the Flue Gas of the Pulping Processes," J. Air Pollution Control Assoc. 22, 790 (1972).

Giever, P., "Control of Emissions from Gray Iron Foundries," American Foundrymen's Society Meeting (October 1970).

Iapalucci, T. L., R. J. Demski and D. Bienstock, "Chlorine in Coal Combustion," U.S. Bureau of Mines Report RI-7260 (1969).

MCA and PHS, "Atmospheric Emissions from Sulfuric Acid Manufacturing Processes," U.S. Dept. HEW, Pub. #999-AP-13 (1965).

McCrone Associates, "Final Report on KPL Field Tests," EPA Contract No. EHS-D-71-25 (1971).

Ryason, J. and R. Harkins, "A Control Technique for SO_2 and NO_x," J. Air Pollution Control Assoc. 17, 1813 (1967).

Smith, W. S. and C. W. Gruber, "Atmospheric Emissions from Coal Combustion," U.S.P.H.S. Report #999-AP-24 (1966).

Varga, A., et al., "A Systems Study of the Integrated Iron and Steel Industry," Contract No. PH 22-68-95 (1969).

West, P. and H. Gaeke, "Fixation of SO_2 as the Disulfitotetrachloromercurate Complex and Subsequent Colorimetric Determinations," Anal. Chem. 28, 1816 (1956).

APPENDIX A

PROCEDURE FOR SAMPLING AND ANALYSIS

I. TEST REQUIREMENTS AND PLANNING

The initial step in the experimental procedure is to establish the velocity, pressure, temperature, and moisture content of the stack gases. Velocity measurements are required to permit integration over the cross sectional area to compute the total volume of the effluent. Industrial and power boilers and heaters are usually designed for exhaust velocities of 2,000-3,000 ft/min, which is a convenient range for pitot tube use. The pitot tube sampling points can be used subsequently for sampling of gaseous pollutants.

II. SOURCE CHARACTERISTICS - PRELIMINARY ESTIMATES

To estimate sampling rates, the expected SO_x concentration may be calculated since sulfur oxide emissions depend primarily on the sulfur content of the fuel. Good correlation has been obtained between SO_2 (the major species) concentrations in the flue gas calculated by stoichiometry and SO_2 measured by manual wet chemical techniques, provided reliable sampling and analytical methods are used. For oil- and coal-fired units, SO_2 concentration may be estimated (within 20%) from the fuel analysis (C,H,S) the fuel feed rate and the amount of excess air. An exemplary calculation is given below.

For the typical residual oil analysis given in Table A-1, the stoichiometric oxygen requirement (no excess air) is shown below. The resulting flue gas composition for 15% excess air is given in Table A-2.

The concentration of SO_2 in the flue gas is seen to be 1270 ppm. For well-controlled combustion at low excess air, SO_3 concentrations may be estimated as about 1% of the SO_2 concentration.

The total flue gas volume per unit weight of fuel consumed is readily obtained from the molar volume at standard (or any convenient) temperature.

$$\frac{\text{Volume flue gas at 60°F}}{\text{ton fuel}} = \frac{56.61 \text{ mole}}{100\# \text{ fuel}} \times \frac{379 \text{ ft}^3}{\text{mole}} \times \frac{2000\#}{\text{ton}} = 430{,}000 \text{ ft}^3$$

TABLE A-1

OXYGEN CONSUMPTION FOR OIL COMBUSTION

Element	Wt. %[†]	Moles[*]	Moles[*] O_2 Needed
C	87.7	87.7/12	7.31
H	10.0	10.0/1	10.0/4 = 2.50
S	2.3	2.3/32	0.0719
		TOTAL	9.88

---

[*] pound moles/100 lb fuel

[†] typical residual oil analysis

TABLE A-2

FLUE GAS COMPOSITION (WET)

Species	Moles[a]		%[b]
CO_2		7.31	12.91
H_2O	2 x 2.50 =	5.00	8.83
SO_2		0.0719	0.127
O_2[b]	9.88 x 0.15 =	1.481	2.62
N_2[b]	9.88 x 1.15 x 3.77[c] =	42.75	75.5
	TOTAL	56.61	100.0

---

a. pound moles/100 lb fuel

b. 15% excess air

c. (nitrogen + argon)/oxygen ratio for dry air

Thus, by preliminary calculation, estimates of sulfur oxide flue gas concentrations and emission parameters may be made to determine initial values for sample volume and flow velocity.

III. SAMPLING COMPONENTS

The following sections describe an integrated modular flue gas sampling apparatus for collection of SO_3 either by absorption in a solution consisting of 80% isopropanol-20% water, or by controlled condensation of the flue gas and collection of H_2SO_4 by filtration, and collection of SO_2 in midget impingers containing dilute hydrogen peroxide solution.

A. PROBE AND PROBE HEATING

The probe (see Figure 1-3) is constructed of a six-foot length of pyrex tube with a 12/5 socket joint on the downstream end. The other end of the probe, which protrudes into the stack, is fitted with a 1.5 inch diameter by 4-cm length of pyrex tube, loosely packed with quartz or pyrex wool for particulate filtration.* The glass probe is inserted into a stainless steel shell with stack adapter assembly which allows various probe insertion depths. The glass probe is wrapped with 20-gauge, asbestos-covered wire to allow heating of the glass insert above the acid dewpoint. The probe is controlled by 120 VAC. This gives a temperature of 150°C with room air pulled through the probe. A stainless steel extension tube permits the sampling point to be extended to ∿ 12 feet. An example of the probe setup with parallel trains is shown in Figure A-1.

B. MIDGET IMPINGERS AND/OR CONDENSER

C. CRITICAL ORIFICE METER OR DRY TEST METER

---

*See modifications to the glass wool filter in Section 2, page 2-14.

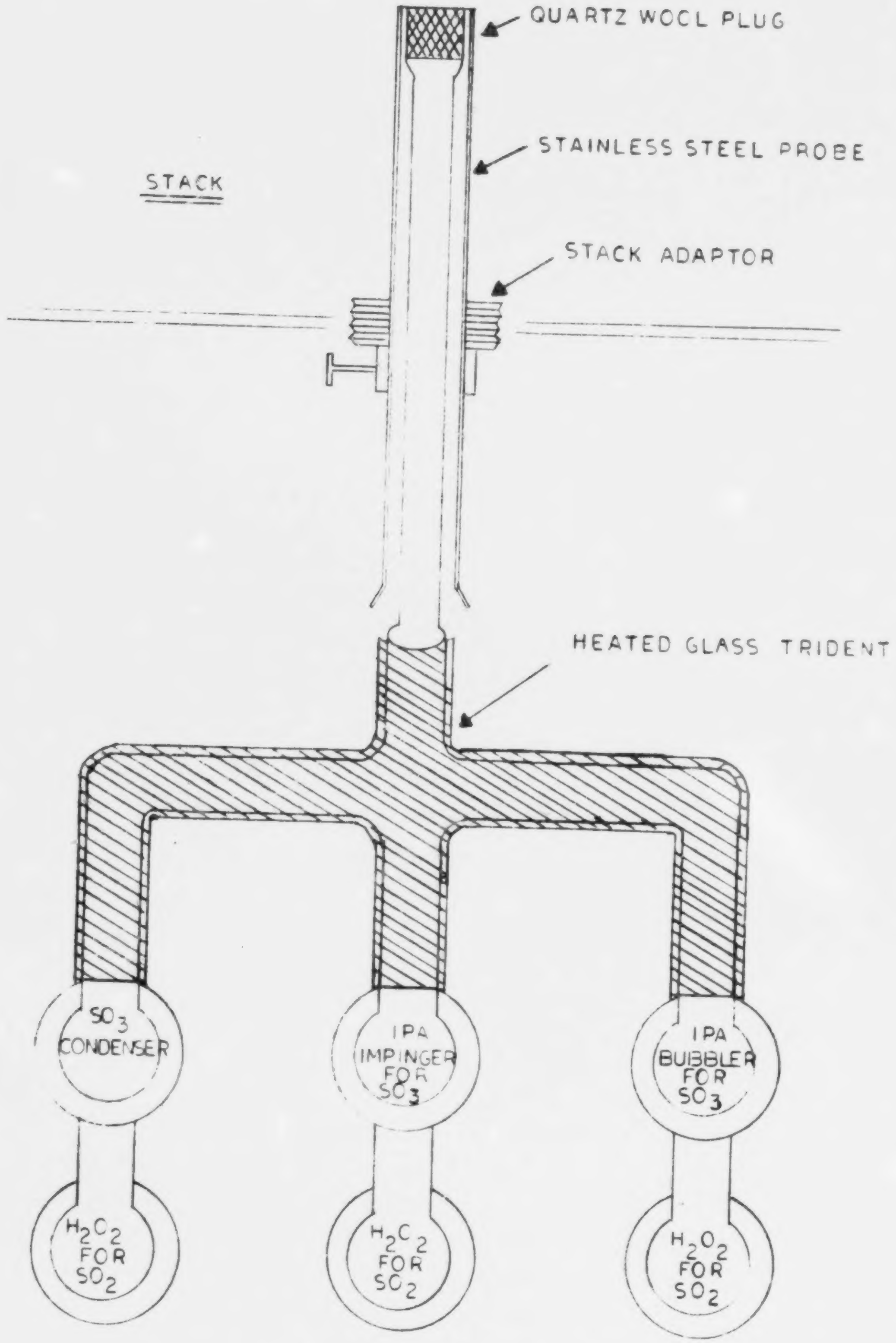

QUARTZ WOOL PLUG
STAINLESS STEEL PROBE
STACK
STACK ADAPTOR
HEATED GLASS TRIDENT
SO_3 CONDENSER
IPA IMPINGER FOR SO_3
IPA BUBBLER FOR SO_3
H_2O_2 FOR SO_2
H_2O_2 FOR SO_2
H_2O_2 FOR SO_2

Figure A-1. Schematic of Parallel Trains Used for SO_3 and SO_2 Collection.

D. ADDITIONAL EQUIPMENT

Stop Watch - For measurement of sampling duration.

Thermometer - A dial thermometer or thermocouple (200-500°F) for measuring the stack gas temperature.

Plastic Bottles - Polyethylene bottles for storage of impinger and condenser samples.

E. REAGENTS

1. Isopropanol-Water (IPA) for SO_3 Collection

Prepare 80% isopropanol by mixing four parts alcohol with one part of sulfate-free distilled water or for rinsing condenser.

2. Hydrogen Peroxide (3%) for SO_2 Collection

Prepare 3% hydrogen peroxide by tenfold dilution of Baker Analyzed (or equivalent) 30% hydrogen peroxide. This reagent should be prepared fresh daily and stored in polyethylene containers.

3. Distilled Water

Sulfate-free distilled water (see Section 4) is required for rinsing out the SO_2 impingers.

IV. FIELD OPERATIONS

A. PREPARATION OF EQUIPMENT

The pressure drop across the orifice should be checked. If $\Delta P <$ 0.5 atm, the carbon vanes in the pump should be replaced. Critical orifice calibration should be checked in the laboratory with a spirometer or gasometer. Examine the particulate filter (glass or quartz wool) in the probe. If this is heavily loaded, it should be replaced. Check heating elements on probe module to ensure that they are operating properly. Check glass equipment for cracks and replace broken components. Make certain that glassware to be used in the field is carefully packed. Check sampling modules for loose connections.

B. SELECTION OF SAMPLING RATES

SO_3 - Collection of SO_3 by absorption in 80% isopropanol was investigated for midget impingers maintained at ice temperatures. The data show that even at flow rates less than 3 liters/min, collection was ∿ 95% for two series impingers. Sampling rates of 3.0 liters/min or less are recommended for SO_3 collection. The collection efficiency of the controlled condensation method for H_2SO_4 has shown to be 97% for flow rates up to 20 liters/min (Driscoll and Berger, 1971).

SO_2 - The collection efficiency of SO_2 absorbed in 3% peroxide solution in midget impingers was determined as a function of concentration (200-2000 ppm), temperature (up to 40°C), and flow rate (0.5-5 liter/min) (Driscoll and Berger, 1971). Over the temperature and concentration range examined, no change in the collection efficiency was observed. With 15 cc of 3% peroxide solution, 96% collection efficiency was obtained at sampling rates of 0.5 and 1 liter/min. Collection efficiency dropped to 90 and 87% at 3 and 5 liters/min, respectively. However, quantitative collection can still be obtained if two series impingers are used. At the highest flow rate (5 liters/min) some blowover and loss of sample occurred. At high concentrations (4000 ppm), a 0.5 liter/min flow rate is recommended while at SO_2 concentrations about 200 ppm, 3 liter/min flow rate and an extended period of time would be recommended.

C. SAMPLE COLLECTION

The probe module is fitted to the stack flue. Power cords are connected between the SO_x probe heater and the variable transformer. The probe is then heated to an operating temperature of 150°C. The SO_3 impingers are filled with 15 cc of 80% isopropyl alcohol. These two impingers are then immersed in an ice bath. The SO_2 impingers are each charged with 15 cc of 3% peroxide solution. After the probe has reached operating temperature, the pump is connected to the last impinger with a vacuum hose and started from the switch on the control module. The time is recorded. The operator checks ΔP across the critical orifice selected (0.5, 1.0, 3.0 liters/min) and records the pressure and temperature value at 5 minute intervals during sampling or alternatively takes the dry gas meter and temperature readings at 5 minute intervals. At the end of a 20-60 minute sampling period (depending on the SO_2 concentration), the pump is switched off and the time is recorded. The impinger train is disconnected from the probe, the ice bath is removed, and clean air is drawn through the impingers for 15 minutes or the H_2SO_4 is removed from the condenser by rinsing with 80% IPA. Collect the SO_3 sample in a polyethylene bottle for transport to the laboratory. Transfer the contents of the two midget impingers (which contain the SO_2 sample) into a polyethylene bottle. Rinse the impingers several times with sulfate-free distilled water and add these washings to the contents of the polyethylene bottle. After the impingers are charged with 15 cc of 3% hydrogen peroxide and 15 cc of 80% isopropanol (or the condenser is at operating temperature 60-70°C), the system is ready for collection of additional samples.

V. ANALYTICAL METHODS

The following sections give a detailed description of the laboratory methods used for SO_2 and SO_3 analysis.

A. LABORATORY REQUIREMENTS FOR BARIUM CHLORANILATE

1. Equipment

a. Shaker, Burrell wrist-action

b. Centrifuge, small clinical type (capable of 2800-3000 rpm)

c. Analytical balance

d. Spectrophotometer for use in the visible region (@ 530 nm)

2. Glassware

a. 2, 5, 10 ml volumetric pipets

b. 25, 50, 100, 1000 ml volumetric flasks

c. 50 ml buret

3. Reagents

a. Deionized water

b. 0.025M H_2SO_4. Add 10 ml of 18M H_2SO_4 (ACS reagent grade) to 600-700 ml of water in a 1000 ml volumetric flask and mix by swirling the flask. Dilute to the mark with water and mix well. Dilute 145 ml of this 0.18M solution to 1000 ml and again mix well. Standardize against anhydrous sodium carbonate.

c. Barium chloranilate (Fisher "certified" or equivalent)

d. Isopropanol (ACS reagent grade)

e. pH 5.6 buffer. Add 50 ml of 0.2M acetic acid (11.4 ml 99% acid in 1000 ml of distilled water) to 500 ml of 0.2M sodium acetate (27.2g reagent grade $NaC_2H_3O_3 \cdot 3H_2O$ in 1000 ml of water).

f. (Approximately) 1N NaOH. Slowly add 40 grams of NaOH (AR grade) pellets to 800-900 ml of water in a 2-liter beaker with stirring until all pellets are dissolved. Dilute to 1000 ml with water and mix well. Store in a polyethylene or polypropylene container.

g. (Approximately) 1N HCl. Add 86.3 ml of 11.6M HCl (ACS reagent grade) to 800-900 ml of water in a 2-liter beaker with stirring. Dilute to 1000 ml with water and mix well. This solution can be stored in glass.

h. 0.05% phenolphthalein. Dissolve 0.05g phenolphthalein in 50 ml ethanol and dilute to 100 ml with water.

i. Anhydrous sodium carbonate (AR grade)

j. Methyl orange indicator, 0.1%. Dissolve 0.1g in 100 ml of water.

B. LABORATORY PROCEDURE FOR BARIUM CHLORANILATE

1. Standardization

a. 0.025M H_2SO_4. Heat approximately 3 grams of AR grade anhydrous sodium carbonate for 4 hours at 250°C to decompose any residual bicarbonate and to remove water. Cool in a dessicator. Accurately weigh 0.115 ± 0.005g of the dried sodium carbonate into each of three 250 ml Erlenmeyer flasks and dissolve the samples in 50 ml of deionized water. Add 2 drops of 0.1% methyl orange and titrate with the 0.025M H_2SO_4 in a 50 ml buret to a color change from yellow to red-orange. A blank of 50 ml deionized water plus indicator should be determined with each set of titrations.

The normality of the 0.025M H_2SO_4 solution is calculated as follows:

$$N = \frac{\text{Wt. of } Na_2CO_3 \text{ in g}}{(A-B)(0.0530)}$$

where A = ml of titrant needed to reach the endpoint

B = ml of titrant needed for the blank

b. Absorbance. A standard curve is prepared by pipetting 0.5, 1, 2, 5, and 10 ml of 0.025M H_2SO_4 into 50 ml volumetric flasks. Add water to the first four to bring all volumes up to about 10 ml. Add 1 drop of phenolphthalein solution, then add 1N NaOH dropwise to the appearance of a pink color. Add 1N HCl dropwise to the disappearance of a pink color. (This will usually require just one drop.) Pipet 5 ml of pH 5.6 buffer into each flask. Pipet 25 ml of isopropanol into each flask. Mix well, then bring to the mark with water, stopper, and again mix well. Pour the contents of each flask into a corresponding 125 ml screw-top shaker flask containing 0.2-0.3g of barium chloranilate. Shake for 20 minutes on a wrist-action shaker, then centrifuge 10-15 ml of this suspension for five minutes at 2800-3000 rpm. Decant the centrifugate into 1 cm cells and read the absorbance versus water at 530 nm. The blank (no sulfate) versus water should read no more than 0.01 to 0.03 absorbance units. Plot the absorbance versus sulfate concentration in μg/ml final solution.

2. Analysis for Sulfur Oxides

Quantitatively transfer the samples collected to a 50 ml volumetric flask (25 ml vol. flask for SO_3). Pipet a suitable sized aliquot into a 50 ml volumetric flask (25 ml volumetric flask for SO_3). Add 1 drop of phenolphthalein solution to the flask, then add NaOH dropwise until the solution just turns pink. Add 1 drop of 1N HCl to return the solution to colorless. Pipet in 5 ml of pH 5.6 buffer (2.5 ml for SO_3 analysis), then add 25 ml isopropanol (12.5 ml for SO_3 analysis) and mix well. Dilute to the mark with deionized water. Pour contents into a 125 ml screw-top shaker flask containing 0.2-0.3g of barium chloranilate. Shake for 20 minutes on a wrist-action shaker. Centrifuge 15 ml of the solution at 2800-3000 rpm for six minutes, decant the solution into 1 cm cells, then read the solution absorbance versus a water blank at 530 nm.

The concentration of SO_2 (SO_3) by volume is calculated as follows:

$$\text{ppm } SO_2\ (SO_3) = \frac{(A)(S)(50)^*(24.1)(50/X)^*}{96\ V_s}$$

where X = volume of sample analyzed

A = absorbance of sample less absorbance of blank

S = slope of calibration curve (μg/ml/Abs unit)

V_s = sample gas volume (STP) = (sampling rate of orifice converted to STP x time)

*for SO_3 analysis use 25 and 25/X, respectively.

C. LABORATORY REQUIREMENTS FOR NaOH TITRATION

1. Equipment

a. Magnetic stirrer and stirring bars

b. Analytical balance

2. Glassware

a. 5, 10 ml volumetric pipets

b. 25, 50, 1000 ml volumetric flasks

c. 50 ml beakers

d. 50, 100 ml graduates

e. 50 ml buret

3. Reagents

a. Deionized water

b. 0.02N NaOH. Slowly add 0.8g sodium hydroxide (AR grade) to 800-900 ml of deionized water. After the pellets are dissolved, dilute to 1000 ml with deionized water and mix well.

c. Bromphenol blue indicator. Dissolve 0.1g bromphenol blue in 7.5 ml of 0.2N NaOH and dilute to 250 ml.

d. Potassium acid phthalate - primary standard

e. Phenolphthalein indicator. Dissolve 0.5g of phenolphthalein in 50 ml of ethanol and add 50 ml of water.

D. LABORATORY PROCEDURE FOR NaOH TITRATION

1. Standardization

Weigh 2-3g of primary standard potassium acid phthalate (KHP) into a weighing bottle and dry in an oven at 120°C for 2 hours. Cool in a dessicator. Accurately weigh three 0.1 ± 0.005g portions of the dried KHP into each of three 250 ml Ehrlenmeyer flasks and dissolve the sample in 50 ml of water. A blank containing no KHP should be run with each set of samples. Add 2 drops of phenolphthalein indicator and titrate with the NaOH to a faint pink color. Compute the normality of the NaOH as follows:

$$N = \frac{\text{g KHP}}{(0.204)(A-B)}$$

where A = ml of titrant needed to reach the endpoint
B = ml of titrant needed for the blank

2. Analysis for Sulfur Oxides

Quantitatively transfer the sample collected to a 50 ml volumetric flask; dilute to the mark with deionized water. Pipet a 5 ml aliquot into a 50 ml beaker, add 2-3 drops of bromphenol blue indicator and titrate to the blue endpoint using the standardized NaOH solution. A blank of 10 ml deionized water and 2 drops indicator should be run with each series of samples.

The concentration of SO_2 (SO_3) by volume is calculated as follows:

$$\text{ppm } SO_2\ (SO_3) = \frac{(A-B)(N/2)(24.1)(10^3)(50/X)}{V_s}$$

where A = ml of titrant needed to reach endpoint

B = ml of titrant needed for blank

N = normality of NaOH solution

X = volume of sample analyzed

V_s = sample gas volume (STP) = (sampling rate of orifice converted to STP x time)

E. LABORATORY REQUIREMENTS FOR Pb^{++} TITRATION

1. Equipment
   - a. Lead electrode (Orion 94-82A)
   - b. pH/MV meter (Orion 701)
   - c. Double junction reference electrode (Orion 90-02)
   - d. Magnetic stirrer and stirring bars
2. Glassware
   - a. 2, 5, 10, 100 ml volumetric pipets
   - b. 50, 1000 ml volumetric flasks
   - c. 250 ml beakers
   - d. 50 ml buret
   - e. 50 ml graduate
3. Reagents
   - a. 0.1M $Pb(ClO_4)_2$ (Orion 94-82-06)
   - b. Methanol (ACS reagent grade)
   - c. Zinc (metal)
   - d. Deionized water
   - e. (Approximately) 1M $NaNO_3$. Add 8.5g $NaNO_3$ to 60 ml of deionized water in a 100 ml vol. flask; swirl to dissolve; dilute to mark.

f. Potassium hydrogen phthalate buffer (pH 4). Add 1.0 ml of 0.1M HCl to 500 ml of 0.1M potassium hydrogen phthalate.

g. Orion 90-00-02 filling solution

F. PROCEDURE FOR Pb^{++} TITRATION

1. Calibration and Standards

Standards are prepared via a series of tenth dilutions of the standard 0.1M $Pb(ClO_4)_2$ (Orion 94-82-06). Standardizing solutions more dilute than 10^{-3}M must be prepared daily. The lead electrode (Orion 94-82A) is used with a double junction reference electrode (Orion 90-02) filled with 1M $NaNO_3$ in the outer chamber and Orion 90-00-02 solution in the inner chamber. The electrode is calibrated by measuring the potential of 10^{-1}M through 10^{-5}M $Pb(ClO_4)_2$ solutions. The potential (MV) is graphed versus the concentration on semi-log paper. The calibration of the electrode should be checked in the desired range prior to beginning analyses.

2. Determination of Sulfur Oxides

Quantitatively transfer the sample collected to a 50 ml volumetric flask and dilute to the mark with deionized water. Pipet a suitably-sized aliquot (2, 5, or 10 ml) in a 250 ml beaker. If pH of solution is greater than 1, acidify with dilute HCl. Add 0.1-0.2g zinc; when pH of sample is 5-6 (5 to 10 minutes), add 5 ml of potassium hydrogen phthalate buffer (pH 4), sufficient deionized water to make a total volume of 50 ml, and 50 ml of methanol (ACS reagent grade). Titrate the sample with standard 0.01M $Pb(ClO_4)_2$, monitoring the titration with the lead electrode. Add the titrant in increments of 0.5 to 1.0 ml in the beginning of the titration and about 0.1 to 0.20 ml in the endpoint region. Record the potential after each addition. Continue the titration 4-5 ml past the endpoint. Stir continuously throughout the titration. Plot ml of $Pb(ClO_4)_2$ versus MV readings on standard coordinate graph paper. The point of greatest inflection is taken as the endpoint. A typical potentiometric titration curve is shown in Figure A-2.

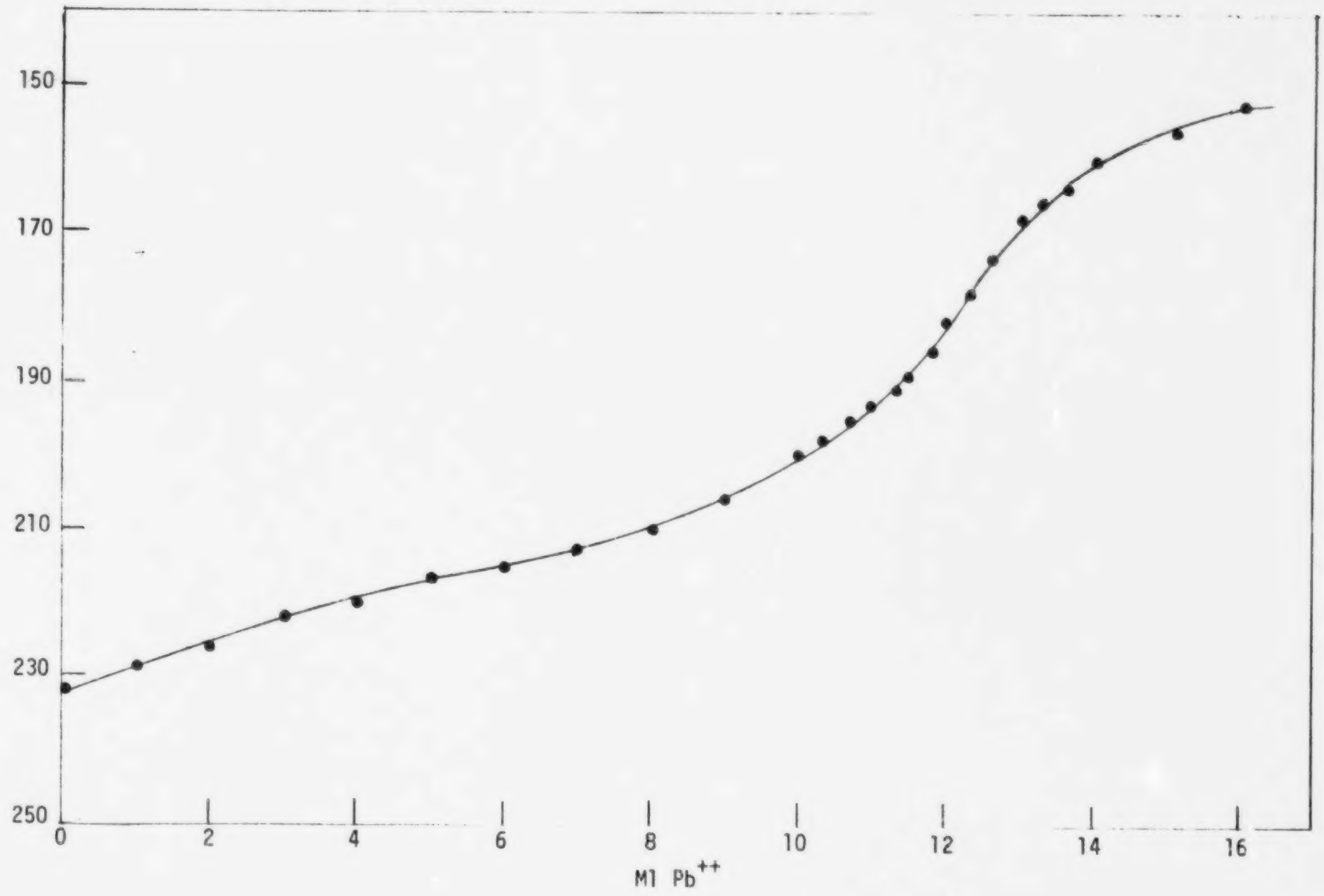


Figure A-2. Potentiometric Titration of Sulfate with a Pb^{++} Ion Selective Electrode.

The concentration of SO_2 (SO_3) by volume is calculated as follows:

$$\text{ppm } SO_2\ (SO_3) = \frac{\text{ml}(M)(0.01)(24.1)(10^3)(50/X)}{V_s}$$

where X = volume of sample analyzed

V_s = volume gas sampled (STP) = (sampling rate of orifice x time converted to STP)

M = molarity of $Pb(ClO_4)_2$ solution

G. LABORATORY REQUIREMENTS FOR Ba^{++} TITRATION

1. Equipment

   a. Magnetic stirrer and stirring bars

   b. Analytic balance

2. Glassware

   a. 2, 5, 10 ml vol. pipets

   b. 100 ml beakers

   c. 25, 50, 100, 1000 ml vol. flasks

   d. 50 ml buret

3. Reagents

   a. Deionized water

b. (Approximately) 1N NaOH. Slowly add 40 grams of NaOH (AR grade) pellets to 800-900 ml of water in a 2-liter beaker with stirring. Dilute to 1000 ml with water and mix well. Store in a polyethylene or polypropylene container.

c. (Approximately) 1N HCl. Add 86.3 of 11.6M HCl (ACS reagent grade) to 800-900 ml of water in a 2-liter beaker with stirring. Dilute to 1000 ml with water and mix well. This solution can be stored in glass.

d. Sulfuric Acid, 0.01N. Dilute 36N ACS reagent grade acid by pipetting 10 ml into a 1000-ml volumetric flask containing 800-900 ml of water. Swirl, then dilute this to the mark with additional water. Accurately dilute 30 ml of this 0.36N solution to 1000 ml by adding the 30 ml to 800-900 ml of water contained in another 1000 ml vol. and, after swirling, make this up to the mark with additional water. Stopper the flask and mix the contents. Standardize the 0.36N solution against anhydrous sodium carbonate.

e. Anhydrous sodium carbonate - AR grade

f. Methyl orange indicator, 0.1%. Dissolve 0.1 gm of the solid in 100 ml of water and filter, if necessary.

g. Isopropanol - ACS reagent grade

h. 0.01M barium perchlorate. Prepare 0.01M barium perchlorate by dissolving 3.9 grams of the solid $Ba(ClO_4)_2 \cdot 3H_2O$ in 900 ml of 80% isopropyl alcohol contained in a 1000-ml volumetric flask. Adjust the solution pH to 3.5 with dilute perchloric acid (several drops of the dilute perchloric usually suffices), then dilute to the mark and mix well. Standardize against 0.01N H_2SO_4.

i. Perchloric acid, dilute. Add 1 volume of 70% AR grade perchloric acid to two volumes of sulfate-free water.

j. Mixed indicator. Two parts 0.2% thorin to one part 0.0125% methylene blue, both solutions in sulfate-free water. Prepare thorin by dissolving 0.2 gm of the solid in 100 ml water. Prepare methylene blue (water soluble variety) by dissolving 0.0125 gm of the solid in 100 ml water.

H. LABORATORY PROCEDURE FOR Ba^{++} TITRATION

1. Standardization

a. 0.36N H_2SO_4. Heat approximately 5 grams of AR grade anhydrous sodium carbonate for 4 hours at 250°C to decompose any residual bicarbonate and to remove water. Cool in a dessicator. Accurately weigh 0.860 ± 0.001 g of the dried sodium carbonate into each of three 250 ml Erlenmeyer flasks and dissolve the samples in 50 ml of deionized water. Add 2 drops of 0.1% methyl orange and titrate with the 0.36N H_2SO_4 in a 50 ml buret to a color change from yellow to red-orange. A blank of 50 ml deionized water plus indicator should be determined with each set of titrations.

The normality of the 0.36N H_2SO_4 solution is calculated as follows:

$$N_1 = \frac{\text{Wt. of } Na_2CO_3 \text{ in g}}{(A-B)(0.0530)}$$

where A = ml of titrant needed to reach the endpoint

B = ml of titrant needed for the blank

The normality (N_2) of the diluted H_2SO_4 solution is thus

$$\frac{30 \times N_1}{1000} = N_2$$

b. 0.1M $Ba(ClO_4)_2$. Pipet 10 ml of standard 0.01N H_2SO_4 into each of three beakers. Add 40 ml of isopropanol and two drops of modified thorin indicator to each beaker. Titrate with the 0.01M $Ba(ClO_4)_2$ to a color change of yellow to pink. A blank of 40 ml isopropanol, 10 ml deionized water, and two drops of indicator should be determined with the set.

The molarity of the 0.01M $Ba(ClO_4)_2$ is calculated as follows:

$$M = \frac{(A-B)(N_2)}{10(2)}$$

where A = ml of titrant needed to reach the endpoint

B = ml of titrant needed for the blank

N_2 = normality of H_2SO_4 solution

2. Analysis for Sulfur Oxides

Quantitatively transfer the sample collected to a 50 ml volumetric flask (25 ml vol. flask for SO_3) and dilute to the mark with deionized water. Pipet an appropriate aliquot (2, 5 or 10 ml) of the dilute sample into each of two beakers. Add 5 ml deionized water, 40 ml isopropanol, and two drops of modified thorin (for SO_3 analysis use 0.2% thorin) to each beaker. Titrate to the pink endpoint with the standard 0.01M $Ba(ClO_4)_2$. A blank should be run with each series of samples.

The concentration of SO_2 (SO_3) by volume is calculated as follows:

$$\text{ppm } SO_2\ (SO_3) = \frac{(A-B)(M)(10^3)(24.1)(50/X)^*}{V_s}$$

where A = ml of titrant needed to reach the endpoint

B = ml of titrant needed for the blank

M = molarity of $Ba(ClO_4)_2$ solution

X = volume of sample analyzed

V_s = sample gas volume (STP) = (sampling rate of orifice x time) converted to STP

*for SO_3 use (25/X) factor.

APPENDIX B

POTENTIOMETRIC DETERMINATION OF SO_2 IN FLUE GASES WITH AN ION SELECTIVE LEAD ELECTRODE

I. INTRODUCTION

Sulfate can be determined potentiometrically by monitoring its titration with Pb^{++} with a lead ion selective electrode (Orion 94-82A). The sample, in 50% methanol, is titrated with standard lead perchlorate, and the electrode potential is measured throughout the titration with an Orion Model 701 digital millivolt meter. The endpoint is determined by plotting ml of titrant added versus the electrode potential. An example of the reproducibility of the lead electrode is given in Table B-1. Note that the columns represent seven different samples. The standard deviation (precision) is quite good. For example, the σ's for the different Pb^{++} concentrations are:

1×10^{-6} Pb^{++} $\sigma = 3.2$ mV
1×10^{-5} Pb^{++} $\sigma = 1.3$ mV
1×10^{-4} Pb^{++} $\sigma = 0.5$ mV

II. CALIBRATION

The lead electrode is calibrated with a series of standards prepared by the dilution of Orion standard 0.1M $Pb(ClO_4)_2$ solution (94-82-06) with deionized water. The calibration curve (Figure B-1) is obtained by plotting the mV reading versus the concentration on semilogarithmic graph paper. The electrode response is Nernstean at lower levels of Pb^{++}, but deviates at higher concentrations due to the increasing difference between activity and concentration.

III. POTENTIOMETRIC TITRATIONS

Standard 0.02396M H_2SO_4 was analyzed using the lead electrode to study the accuracy of potentiometric titrations for sulfate determinations. All titrations were run in 1:1 mixtures of methanol and water to decrease the solubility of the $PbSO_4$ formed. A typical curve is given in Figure B-2. The H_2SO_4 solution was determined to be 0.02400M which agreed well with the 0.02396M value determined with both sodium carbonate standardization and titration with standard NaOH.

TABLE B-1

REPRODUCIBILITY OF THE ORION ION SELECTIVE (Pb)
ELECTRODE ON CALIBRATION STANDARDS

Sample	Millivolts 1	2	3	4	5	6	7	ΔmV
"mud"*	-236†	-275	-262	-268	-266	-240	-255	
1 x 10^{-6}M Pb^{++}	-222	-225	-224	-226	-226	-217	-224	36
1.1 x 10^{-5}M Pb^{++}	-186	-188	-188	-189	-188	-186	-186	36
1.1 x 10^{-4}M Pb^{++}	-159	-160	-160	-160	-160	-160	-159	28

---

*Blank containing 50% deionized water-50% methanol

†Not used in calculation of Δ

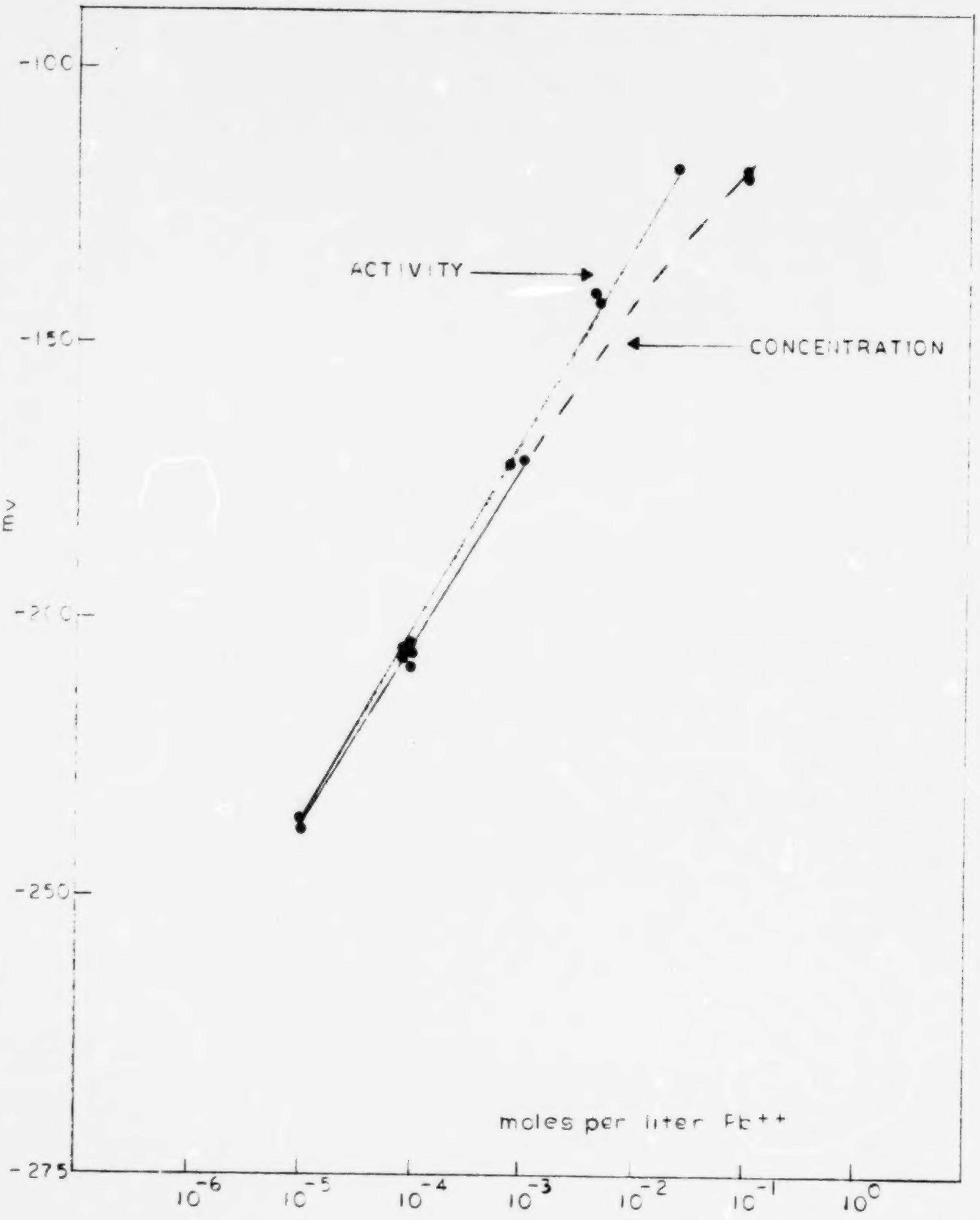


Figure B-1. Calibration Curve Pb^{++} Electrode.

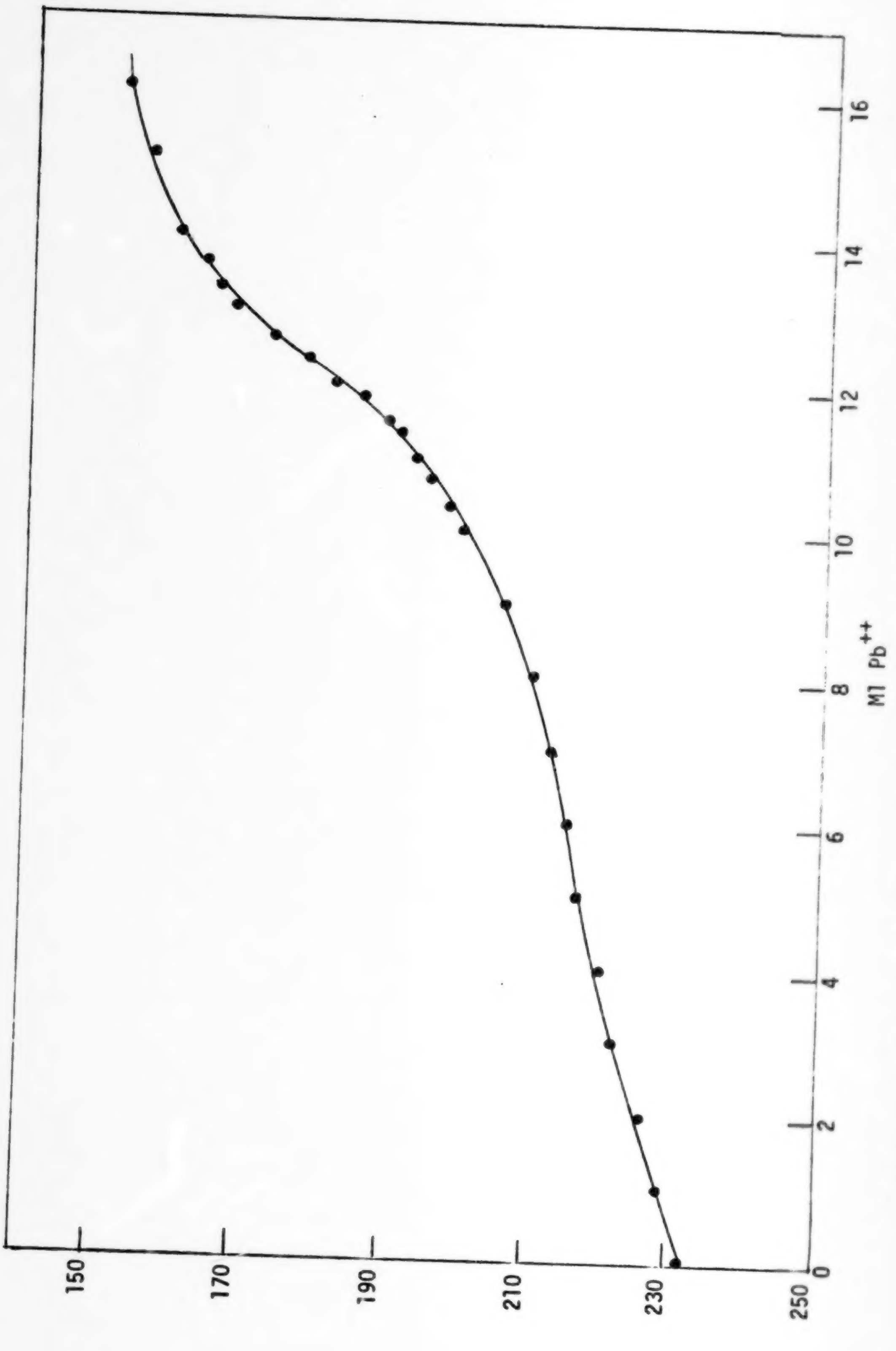


Figure B-2. Potentiometric Titration of Sulfate with a Pb^{++} Ion Selective Electrode.

IV. APPLICATION TO ANALYSIS FOR SULFUR OXIDES IN STATIONARY SOURCES

In addition to the various cations present in effluent samples which interfere with titrations monitored by the lead electrode, e.g., Cu^{++}, Hg^{++}, and Ag^{+} at any concentration, and Fe^{+3} and Cd^{++} at concentrations greater than that of Pb^{++}, there is also a very major interference inherent in the sample collection liquid, e.g., H_2O_2. Sulfur dioxide is collected in 3% hydrogen peroxide which oxidizes the $SO_3^{=}$ to $SO_4^{=}$; H_2O_2 will also oxidize the surface of the electrode, causing erratic response and non-reproducible results.

Initially, heating the solutions was attempted as a means of decomposing the peroxide; this did not decompose all of the peroxide, since subsequent analyses of the solutions indicated that oxidation of the surface of the electrode was still occurring.

A half reaction was sought which would have sufficient potential to reduce the peroxide to water, but not interfere with the Pb^{++} titration. The Zn/Zn^{++} couple was selected (Table B-2). Zinc metal (0.1-0.2g) was added to a sample prior to its analysis. Completion of the reduction of peroxide was noted by a decrease in pH from approximately 1 to 6. Potassium hydrogen phthalate buffer (pH 4) was added to the sample to prevent precipitation of Zn $(OH)_2$, which occurs at pH 6. The Zn/Zn^{++} also will reduce the other cations known to poison the lead electrode (Table B-2), thereby removing all major interferences to the titration. Titrations performed using this method yielded accurate and reproducible results which compared well with values found using standard methods for SO_2 analysis (Table B-3). A typical curve for a sulfuric acid plant sample is seen in Figure B-3.

An alternate method of assimilating data is the use of Gran's plots (Gran, 1952). These plots involve plotting ml of titrant vs potential (mV) on semi-antilog paper which is designed to accommodate the volume change which occurs during the titration. The basis for this selection of axes is Nernst's equation:

TABLE B-2

STANDARD HALF-CELL ELECTRODE POTENTIALS

Ion-Electron Half Reaction	E^o, volts
$H_2O_2 + 2H^+ + 2e = 2H_2O$	+1.77
$Hg^{++} + 2e = Hg$	+0.854
$Ag^+ + e = Ag$	+0.799
$Fe^{+++} + e = Fe^{++}$	+0.771
$Cu^{++} + 2e = Cu$	+0.337
$Pb^{++} + 2e = Pb$	-0.126
$(Ca^{++} + 2e = Cd$	-0.403)
$Zn^{++} + 2e = Zn$	-0.763

TABLE B-3

SO_2 TEST RESULTS - COMPARISON OF ANALYTIC METHODS

Sample No.	ppm SO_2 (Pb^{++})†	ppm SO_2 (Pb^{++}-Gran's Plot)	ppm SO_2 (Ba^{++})	ppm SO_2 (Ba Chlor)	Source
3B	--	1089	1049	1122	Sulfuric Acid Plant
7A	--	825	1135	1089	Sulfuric Acid Plant
13B	1115	1149	1090	1098	Sulfuric Acid Plant
14A	--	1113	1113	1096	Sulfuric Acid Plant
15C	--	620	947	848	Sulfuric Acid Plant
16A	866	1228	882	765	Sulfuric Acid Plant
25A	--	811	1054	1032	Sulfuric Acid Plant
36C	975	1202	1084	--	Sulfuric Acid Plant
40C	--	227	827	687	Sulfuric Acid Plant
52B	1165	1435	1266	1234	Sulfuric Acid Plant
54A	1100	1216	1315	945	Sulfuric Acid Plant
56A	1183	1244	1215	1139	Sulfuric Acid Plant
50A	1691	2639	2172	2220	Pb Smelter
52A	4754	--	4822	4696	Pb Smelter
54B	4769	--	5014	4898	Pb Smelter
6B	217	--	238	245	Iron & Steel Plant
11A	--	237	170	172	Iron & Steel Plant
11B	147	146	136	135	Iron & Steel Plant
12B	--	264	140	135	Iron & Steel Plant
12C	--	274	176	165	Iron & Steel Plant
13B	--	146	116	99	Iron & Steel Plant
13C	--	109	118	115	Iron & Steel Plant
29C	--	319	28	38	Iron & Steel Plant
41B	--	155	29	34	Iron & Steel Plant
58A	13	--	14	8	Kraft Mill
59A	35	--	4	21	Kraft Mill
59B	34	--	38	24	Kraft Mill
F13C	498	--	600	--	Coal-Fired Power Plant
F15C	612	--	635	--	Coal-Fired Power Plant

---

†Endpoint determined potentiometrically

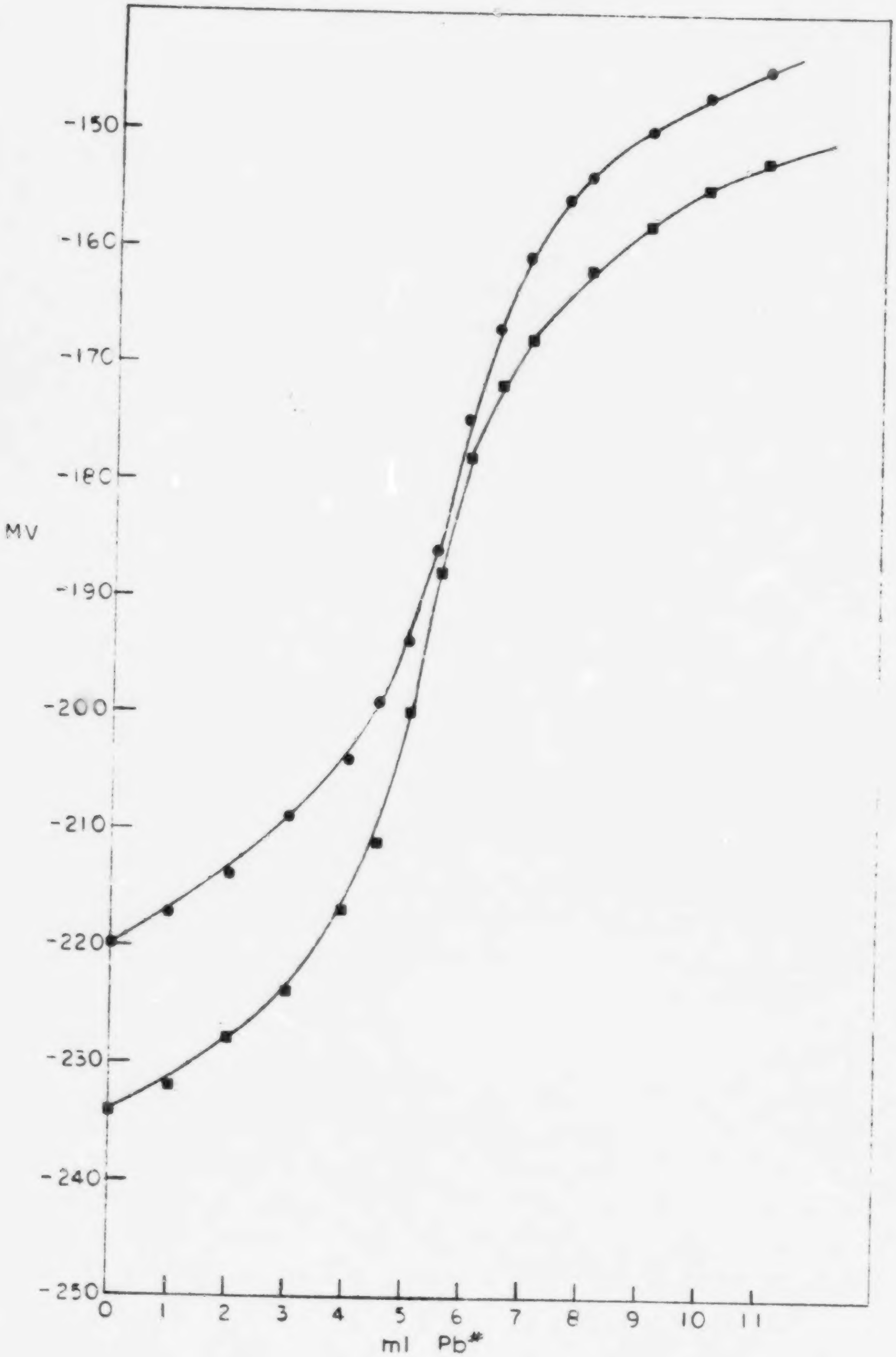


Figure B-3. Potentiometric Titration Curves for SO_2 Samples from a Sulfuric Acid Plant.

$$E = E^{o} + \frac{RT}{nF} \log [A^{-}]$$

Rearrangement yields

$$\frac{nFE}{RT} = \left(\frac{nFE^{o}}{RT}\right) + \log [A^{-}]$$

The ion sensed can be made a linear function of the electrode potential by taking the antilog of both sides:

$$\text{antilog } (E/S) = E_1 + [A^{-}]$$

where $S = nF/RT$ and $E_1 = \text{antilog } (E^{o}/S)$

The change in volume is corrected for, as previously mentioned, by shifting the axis up 10% from left to right making additions of up to 10% of the original sample volume possible. Gran's plot paper has a slope of 58 mV for a monovalent electrode and 29 mV for a divalent electrode. Corrections for electrodes whose slopes differ from 58 mV can be achieved by the use of a blank.

A major advantage to the use of Gran's plot paper (available from Orion Research Corp.) is that the plot is linear, hence fewer points are needed and the time per determination is reduced considerably. A straight line is drawn through the points and the endpoint is found by extrapolation to the x axis. With this method, points well beyond the endpoint can be used to obtain the straight line and thereby the endpoint.

One difficulty which arises from the addition of zinc to the sample to be analyzed is that Pb^{++} is reduced as well as the interfering cations. This will cause points after the endpoint to be questionable. This could affect the potentiometric curve by varying the slope in the endpoint region. Apparently, this reduction does not occur rapidly at low levels of excess Pb^{++} and the potentiometric curve still yields accurate results. Regression equations using the Ba^{++} titration and Ba Chloranilate methods as standards give excellent correlation coefficients, small intercepts, and slopes near unity (Table B-4). A regression of the Ba^{++} titration vs the Ba Chloranilate method yields comparable results.

TABLE B-4

REGRESSION EQUATIONS

Methods Compared	Regression Equation	Correlation Coefficient
Pb^{++} Titration (Gran's Plot)(x) vs Ba^{++} Titration (y)	y = 0.854 x +95.6	0.926
Pb^{++} Titration (Gran's Plot)(x) vs Ba Chloranilate (y)	y = 0.847 x +62.4	0.936
Pb^{++} Titration (x) vs Ba^{++} Titration (y)	y = 1.04 x +41.4	0.997
Pb^{++} Titration (x) vs Ba Chloranilate (y)	y = 1.02 x +3.6	0.995
Pb^{++} Titration (x) vs Pb^{++} Titration (Gran's Plot)(y)	y = 1.47 x -233	0.939
Ba^{++} Titration (x) vs Ba Chloranilate (y)	y = 0.976 x -18.2	0.998

Gran's plots are, however, much more sensitive to the points after the endpoint; slight variations can greatly affect endpoint determination which is based upon extrapolation. This causes a loss in accuracy which can be seen in the regression equations (Table B-4). The correlation coefficients while still high are lower than those for the Pb^{++} titrations with the endpoints determined potentiometrically. The slope varies ∿ 15% from unity indicating a loss in accuracy of the SO_2 levels determined using Gran's plots. The use of an alternate reducing agent for peroxide, which would not reduce Pb^{++}, might improve the feasibility of using Gran's plots in stack gas SO_2 analyses.

APPENDIX C

SOLID SORBENT STUDIES

The efficiency of several solid sorbents was investigated in the laboratory by passing a gas mixture (SO_2 in nitrogen) through a packed tube containing PbO_2 or ascarite. The sorbent tube was followed with an impinger containing aqueous 3% hydrogen peroxide. The collection efficiency was determined by

$$\frac{\text{ppm } SO_2 \text{ In-ppm } SO_2\text{-impinger}}{\text{ppm } SO_2 \text{ In}} \times 100$$

and is given in Table C-1. Both the PbO_2 and ascarite show very high collection efficiency at room temperature. The Rhom and Hass Amberlite XE309 resin was investigated at a sulfuric acid plant. The inlet SO_2 concentration was calculated from the average of the two peroxide impingers run in parallel with the train. The SO_2 passing the ion exchange resin was measured by placing a peroxide impinger behind the sorbent tube. These data are given in Table C-1.

The purpose of the solid sorbent tests at the sulfuric acid plant was to investigate the feasibility of using the ion exchange resin to collect SO_2 and SO_3 simultaneously. Some preliminary tests by Allied Chemical Corp. with this sorbent system spurred this work. In their work, they found that SO_2 could be desorbed by passing hot gas over the sorbent. The resulting gaseous SO_2 was collected in aqueous hydrogen peroxide. The SO_3 was desorbed by pouring the ion exchange resin in an aqueous solution. They analyzed the sulfate (SO_2 and SO_3) by titration.

In our tests, we found that the SO_2 could be collected quantitatively but we *could not quantitatively desorb* the SO_2 from the resin. We tried passing hot nitrogen over the sample and recovered 5 to 10%. *We could not recover the remaining* SO_2 *by either leaching with water overnight or leaching with boiling water.*

The recovery for the laboratory tests on PbO_2 was also low as indicated in Table C-2. Only the recovery with ascarite was quantitative. Some of the problem with quantitative recovery was the minimal amount of time allotted to this task. We would expect that with some additional effort, SO_2 could be quantitatively removed from these other sorbents.

TABLE C-1

COLLECTION EFFICIENCY DATA FOR SOLID SORBENTS

Sorbent	Length (cm)	Collection Efficiency	No. of Runs	Inlet SO_2 Concentration	Site
PbO_2	15	99	3	330	Laboratory
	10	99	3	330	Laboratory
	5	98	3	330	Laboratory
Ascarite	15	99	3	330	Laboratory
	10	99	3	330	Laboratory
	5	98	3	330	Laboratory
Amberlite XE309	20	98	2	1100	Sulfuric Acid Plant
	15	92	3	1100	Sulfuric Acid Plant
	10	91	5	1100	Sulfuric Acid Plant

Sampling rate = 0.5 liter/min for 15 minutes

Sorbent tubes were made of 8 mm o.d. glass tubing

T = about 20°C

TABLE C-2

RECOVERY FROM SORBENTS

Sorbent	SO_2 Recovery (%)	Procedure
Amberlite XE309	10	(a) hot N_2 then absorption in H_2O_2
	--	(b) aqueous leaching
PbO_2	20	Boiling with Na_2CO_3 followed by acidification, evaporation and Ba Chlor analysis.
Ascarite	105	Leached with aqueous H_2O_2, neutralized with HCl, then analysis by Ba Chlor.

These tests were only preliminary but the collection of various gases on solid sorbents appears promising. More work is needed on the analytical methods and quantitative desorption of these species from the sorbents.

APPENDIX D

PRECISION OF BARIUM ION TITRATION AND BARIUM CHLORANILATE FOR VARIOUS ANALYSTS

The precision of the Ba^{++} titration for six different analysts is given in Table D-1. The precision for two analysts (A and C) for foundry effluents is 3.1 ± 0.3% for SO_2 analysis from foundry effluents. Similarly, A and B have CV's of 1.5 and 1.95%, respectively, for copper smelters. A and F have CV's of 1.5 and 2.0%, respectively, for the uncontrolled coal-fired power plant. Note, however, that B and E have considerably different CV's for the sulfuric acid plant. The CV's of 1.6 and 2.4 by analysts B and D are well within the precision expected at 1000 ppm while the CV of 3.4 by operator E is very poor compared to any other operators or sources at that concentration of SO_2. This analyst appears to have a major problem with *analytical technique*, not just the barium ion titration since the same operator (operator C, Table D-2) has a very high CV on the sulfuric plant with the barium chloranilate where the judgment error associated with the titration is eliminated.

The precision of the other five operators falls between 1.5 and 2.8% regardless of source and/or concentration. The pooled CV (weighted for sample size) for the Ba^{++} titration was 2.1% for the 693 samples in Table D-1.

The precision of the barium chloranilate as a function of analyst is given in Table D-2. Here we don't have as many comparisons on the same source as we did with the barium titration. For an iron and steel plant, analysts A and B get the same precision although the SO_2 levels are different. Analyst C's results (CV's) on the sulfuric acid plant are considerably higher than those obtained by analyst B. This is apparently a problem with analytical technique as mentioned above. The CV for the barium chloranilate method range from 1.7 to 3.5% when no interferences are present or the concentration is greater than 100 ppm. The pooled CV weighted for sample size for 179 samples in Table D-2 is 2.7%. The values below 100 ppm were dropped along with the data from the iron and steel plant. This value of 2.7 is very close to the average values obtained at all the power plant sites by the barium chloranilate method.

The data in this section do provide some limited information on the precision of both methods as a function of operators.

TABLE D-1

COMPARISON OF PRECISION OF Ba^{++} TITRATION FOR SO_2 BY DIFFERENT ANALYSTS

Analyst	Site	No. of Samples	mean ppm SO_2	CV (%)
A	Foundry	24	62	2.8*
	Cu Smelter	30	3181	1.5*
	Uncontrolled Coal-Fired Power Plant	11	432	1.5
B	Cu Smelter	42	3234	2.0
	Cu Smelter	24	3538	1.9*
	Iron and Steel Plant	52	256	1.2
	Iron and Steel Plant	32	214	1.5*
	Pb Smelter	48	3678	1.6*
	Sulfuric Acid Plant	78	1109	1.6
C	Foundry	28	64	3.4*
D	Sulfuric Acid Plant	198	1170	2.4
	Pilot Plant (HCl doping)	12	607	2.0
E	Sulfuric Acid Plant	56	862	3.2
F	Controlled Coal-Fired Power Plant	10	727	2.2
	Oil-Fired Power Plant	22	393	2.3
	Uncontrolled Coal-Fired Power Plant	26	406	2.0

---

*With fine particulate filter in sampling train

TABLE D-2

COMPARISON OF PRECISION OF Ba CHLORANILATE METHOD FOR SO_2 BY DIFFERENT ANALYSTS

Analyst	Site	No. of Samples	mean ppm SO_2	CV (%)
A	Iron and Steel Plant	72	37	4.3*
	Iron and Steel Plant	150	39	3.7
B	Iron and Steel Plant	32	223	4.6*
	Sulfuric Acid Plant	56	1119	2.3
	Cu Smelter	16	3434	1.7*
	Cu Smelter	42	3777	2.3
C	Sulfuric Acid Plant	226	1124	5.6
D	Pilot Plant (HCl doping)	17	220	3.8
E	Controlled Coal-Fired Power Plant	5	701	4.3
	Oil-Fired Power Plant	24	406	3.4
	Uncontrolled Coal-Fired Power Plant	19	460	3.1

---

[*] With fine particulate filter in sampling train